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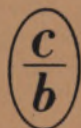
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LITHOLOGY AND MINERAL RESOURCES

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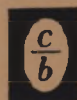
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THE SYSTEMS APPROACH IN LITHOLOGY: INITIAL PREMISES, POSSIBILITIES, AND PERSPECTIVES. REPORT II. THE SYSTEMS APPROACH AS APPLIED TO THE LITHOLOGY AND GENESIS OF OIL AND GAS RESERVOIRS

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The foundations of the natural goal-oriented approach and the theoretical basis of the systems approach to the lithology and genesis of oil and gas reservoirs are presented. The characteristics of system structure, history, function, and lithology are developed, and a foundation is laid which describes the hierarchy of natural geological objects and which necessitates the separation of the lithological – genetic and the oil and gas branches of the hierarchy. The structure and historical development of the Precaspian reservoir is examined. Finally, new principals for determining oil and gas zoning and a method of geological and geophysical study of sedimentary reservoirs as whole natural systems is presented.

BASIC PRINCIPLES OF THE NATURAL GOAL-ORIENTED APPROACH

In today's geology three approaches to the use of a system approach are forming. These approaches are best expressed in the conception of the naturalness of geological systems which contradicts the conception of nominally oriented systems, and which has recently been actively developed in light of the system-active approach. In all of the three approaches there is much merit which without doubt will increase the effectiveness of the system approach in geology.

The natural (naturally objective) and oriented (model oriented) methods basically reflect two approaches to the study of objective reality. The first approach leads the investigator to an understanding of the laws governing the structure of the material world. However, it is not constructive in the sense of obtaining final results quickly since it assumes that all objects should be studied in the form in which they are given by nature. The second approach, on the contrary, is very dynamic and has very clearly defined goals. At the same time, this approach is, to a large degree, oriented toward the solution of practical problems, and is not oriented toward an understanding of the fundamental laws governing the structure of the material world. One should not separate these two approaches, but, instead should use them in combination in order to better understand complex geological formations. Evidently, it would be advantageous to unite the best aspects of these two approaches into a single natural goal-approach which would include the active methods of the system – active approach.

The natural goal-oriented approach has great perceptual possibilities and is practical. The initial premises of the natural goal-oriented approach are as follows:

- the possibility that there exists whole natural systems which orients the study toward an understanding of the laws governing the material world;
- the necessity of an objective in studying natural systems which rationalizes the investigative process;
- the active role of perceived subject which provides a basis for a system organization of the practical activity.

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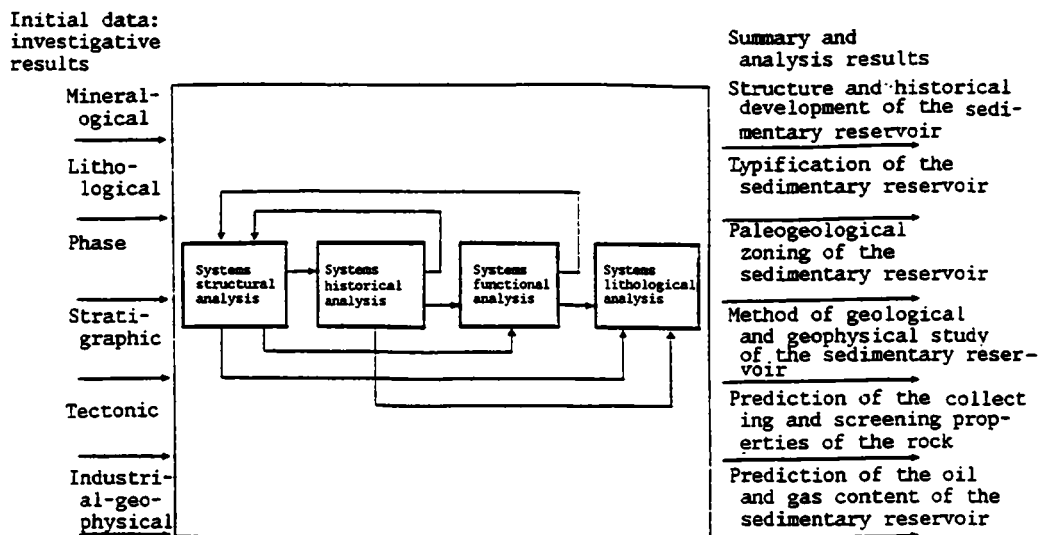


Fig. 1. The lithogenetic systems analysis of oil and gas sedimentary reservoirs.

When using the natural goal-oriented approach objects of nature and the practical activity can be presented as system objects. However, in constructing the objects, it is necessary to always relate them to reality. It should always be remembered that the objects used have a definite limitation to their overall collection of properties, and that only those properties can be used which have been obtained from objective reality. It should also be remembered that the structure will be true if the essential properties of the object have been properly chosen. Here the main criterion is practice which helps to choose from a multivelocity of Properties those which are most characteristic of the object under study, correctly formulate the goal of the investigation, and correlate the object with material reality. Consequently, in developing a system plan of the object it is necessary to be guided by a fundamental knowledge of the material world and also to develop such knowledge. This is possible if it is based on the conception of a law-governed structure in objective reality, and on the presence of wholistic natural systems. The latter act as facts which can be used to establish the laws which govern the structure of the material world. This is the fundamental problem of geological system investigations.

The system pair, resulting from the basic premises of the natural goal-oriented approach (the wholistic natural system and its system model), form a dynamic unity. It possesses a large number of perceptual possibilities since, in the first place, it directs the investigator toward a knowledge of the laws governing the structure of objective reality and in so doing gives such an orientation to the study; secondly, it rationalizes the investigative process and enables one to clearly determine the overall aim; and, thirdly, it has a practical aspect which ensures that adequate and constructive knowledge of objective reality is obtained. In the context of the proposed system developments the principle of a unified theory and practice should be supplemented by an adequate correlation between system structures of theoretical knowledge and those of the material world.

THEORETICAL FOUNDATIONS OF A LITHOGENETIC SYSTEMS ANALYSIS OF OIL AND GAS SEDIMENTARY RESERVOIRS

The main tasks of a lithogenetic systems analysis are to study sedimentary reservoirs as wholistic natural systems, to establish their structures, compositions, genesis, and degree of development, to carry out structural and lithological typifications, and, on this basis, to predict their oil and gas content. The inherent characteristic of such an analysis is that it is a generalized study of sedimentary reservoirs from a lithogenetic point of view. This permits one to develop the basics of the paleozoning and to develop a geological and geophysical systems methods to study sedimentary reservoirs.

The systems analysis is characterized by multiplicity and can be divided into a systems structural, systems historical, systems functional, and systems lithological studies (Fig. 1).

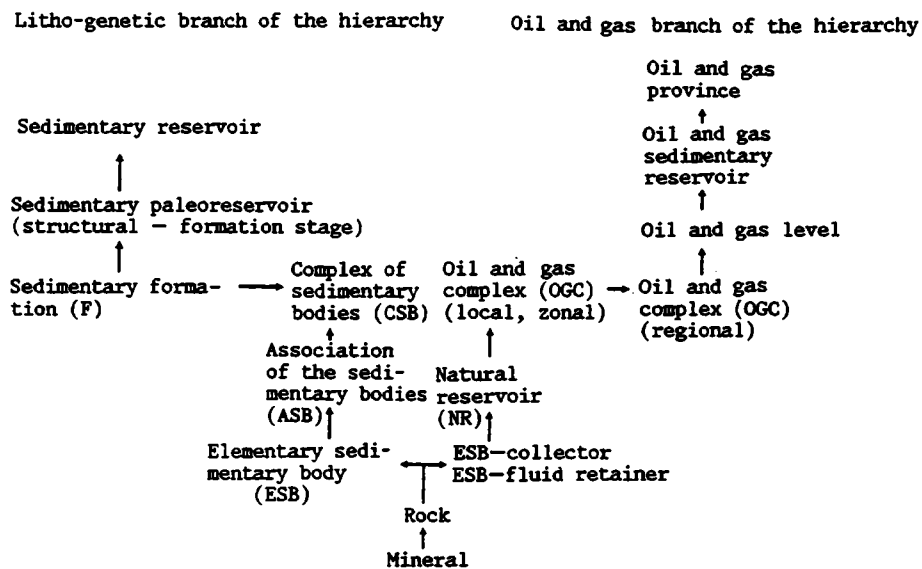


Fig. 2. The hierarchy of natural geological objects.

In carrying out a lithogenetic systems analysis of oil and gas sedimentary reservoirs it is necessary to distinguish three consecutive stages in the study. The first stage is based on the results of a systems structural and systems historical study whose goals are to establish the structure of the sedimentary reservoir and the history of its geological development. The second stage incorporates the study of natural reservoirs, their collecting and screening properties, and is based on the results of systems lithological and systems functional investigations. The main goal of the third stage is to predict the oil and gas content of the sedimentary reservoir under study.

At this stage the lithogenetic systems analysis is directed toward solving the practical problem of uncovering the most perspective areas of the sedimentary reservoir for oil and gas recovery.

The systems structural study establishes the structure and determines the nature of the associations between the different elements which ensure the wholeness of the system during its existence, functioning, and development. In this context, structures can be divided into static structures, which explain the structural laws governing the system, and into dynamic structures, which determine the behavior of the system during its functioning and development.

In system studies structural hierarchy has received widespread recognition. On the one hand, this can be explained by the fact that a hierarchical structure is the most effective for organizing data concerning the behavior of an object into operational knowledge. On the other hand, hierarchical structures arise naturally during the process of an evolutionary formation of the complex from the simple while maintaining intermediate forms of development [11].

In studying complex geological formations it is necessary to maintain correspondence between the systems structural and systems historical studies. The systems structural analysis enables one to divide the system into elements, to study the interrelations between these elements, and to propose a structure for the geological object under study. However, one can not come to know such a complex system as a sedimentary reservoir through a single structure. The combination of the systems structural and systems historical studies enables one to not only establish the successiveness of the occurrences, whose results lead to the formation of the sedimentary basis, but to also determine its genesis and evolution. This in turn leads to an overall picture of the sedimentary reservoir as an historically developing system.

In examining sedimentary bodies the main historical-geological associations involved in sedimentary formation and developed by G. P. Leonov [10] are used.

An elementary sedimentary body (ESB) is a monorock body or a number of monorock bodies which are similar in composition and which form a system whole at a unique place. They formed at a similar time and under similar conditions of sedimentary accumulation (unstable local physical and geomorphological circumstances). The ESB differs from neighboring elementary bodies by a number of indications and their combination, and also by a combination of rock types and their relationships.

In carrying out a systems structural and systems historical analysis of sedimentary bodies objects are distinguished whose subsequent grouping has two main goals:

to reestablish the developmental history of the sedimentary reservoir, its evolution in space and time, the conditions of sedimentary accumulation, and the tectonic and climatic conditions at each stage in the development of the reservoir;

to establish the characteristic oil and gas content of the sedimentary reservoir, the changes in the collecting and screening properties of the rock, and the conditions of hydrocarbon generation and accumulation.

In order to solve the first task the objects placed in the lithogenetic branch of the hierarchy are distinguished in such a way that they mainly differ from each other in scale (Fig. 2).

Association of sedimentary bodies (ASB) is a name for the combination of ESB which are located at one place and formed under identical conditions of sedimentary accumulation (stable physical – geomorphological circumstances). These ASBs differ from each other by their combinations of ESB and by the way in which these ESBs relate to each other.

The complex of sedimentary bodies (CSB) is a name for the combination of ASBs which are located in one place and time and under identical conditions of sedimentary accumulation (topographical and paleogeographical circumstances). These CSB differ from each other by their combination of ASBs and by the way in which these the ASBs relate to each other. The CSBs occupy a section of the sedimentary reservoir which corresponds to a definite topographical and paleogeographical setting, and to that cross section of the sedimentary rock which formed under given landscape and climatic conditions. The necessity to distinguish the complex of sedimentary bodies is due to the fact that one and the same tectonic and climatic conditions can be differently reflected in the sedimentary body taking shape depending on the topographical and paleogeographical setting.

The formation of the sedimentary body is a name for the combination of CSBs which have come together at a unique point in space and time and under identical conditions of sedimentary accumulation (landscape and climatic setting). The formation occupies the whole area of the sedimentary reservoir, and has, as a rule, a "ragged" structure. This corresponds to the various topographical and paleogeographical settings of sedimentary accumulations. They form under identical tectonic and climatic conditions which are variously expressed (lithological composition and structure) in different sections of the reservoir in the form of the complex of sedimentary bodies.

A similar path to sedimentary formation corresponds to the one developed by N. M. Strakhov [12]. It differs by having a more clear limitation to the expansion of the formation. The formation of N. M. Strakhov does not expand due to the fact that it occupies a too vast and undefined territory.

The introduction of a complex of sedimentary bodies into the reservoir structure, which is a part of the formation and which reflects the different topographical and paleogeographical settings of sedimentary accumulation, eliminates the objections of N. S. Shatsk and N. P. Kheraskov to the genetic principles of formation deposition.

In the cross section of the sedimentary cover of a reservoir structure levels often precipitate which are fixed along nonconformities. They may include one or several formations. The structural formation levels reflect a definite stage in the development of the section of the earth crust under study, and correspond to an ancient sedimentary reservoir (paleo-reservoir). During an increase in the intensity of tectonic movement and during active upheavals, there is, as a rule, a change in the boundaries, volume, and overall shape of the formation.

The sedimentary reservoir is the highest level in the lithogenetic branch of the hierarchy. This object is a combination of formations united at a single geotectonic position of the earth's crust.

In solving the second task, objects precipitate which have significantly different properties. These objects form the oil and gas branch of the hierarchy (see Fig. 2). The initial element of this branch is also an elementary sedimentary body (ESB). The combination of ESB collectors and ESB fluid retainers leads to the formation of a system with clearly defined properties. This system has the ability to accumulate hydrocarbons and to prevent them from dispersing. A natural reservoir (NR) is a single system of two objects which differ in their ability to filtrate fluids collecting rocks and fluid formation rocks. The separation of one object from the other leads to a disintegration of the system.

A NR is incorporated into an oil and gas complex (OGC). If the OGC contains an oil and gas producing deposit, it can be viewed as a system possessing a new property. This property is the ability to generate and accumulate hydrocarbons.

An OGC which contains an accumulation of hydrocarbons within the boundaries of the formation and in the zone of oil and gas accumulation is called a local and zonal oil and gas complex respectively. An OGC in which there is an accumulation of oil and gas in the whole or in a large part of the sedimentary reservoir is called a regional oil and gas complex [2].

An OGC which is located within the limits of a structural-formation level (paleoreservoir) develop its own level of oil and gas content. A sedimentary reservoir containing an accumulation of oil and gas is called an oil and gas sedimentary reservoir. It occupies the highest level in the oil and gas branch of the hierarchy.

The delineation of objects into a hierarchy along with a systems structural study enables one to complete a systems historical analysis. It also enables one to establish the association between the elements and in this way to clarify the successive geological occurrences which led to the initial precipitation of the sedimentary body. Finally, it reestablishes the conditions of its formation and the history of the geological development of the sedimentary reservoir.

STRUCTURE AND HISTORICAL DEVELOPMENT OF THE PRECASPIAN SEDIMENTARY RESERVOIR

As was pointed out in the previous section, separate formations form under unique tectonic and climatic conditions, and expand within the limits of the whole area of the sedimentary reservoir. A different topographical and paleogeographical setting for the sedimentary accumulation can lead to dissimilar material in the developing formation. This forces one to divide it into a complex of sedimentary bodies, which, consequently, are parts of the formation and occupy an area of the sedimentary reservoir. It is important to emphasize that the formation in this context is a structurally separable sedimentary reservoir.

The study of formations as large geological bodies gives information the tectonic and climatic evolution of the sedimentary reservoir which should be "embedded" in their denomination. For the tectonic characteristics of formations it was proposed in [8] to use the phases of S. N. Bubnov [4], and to differentiate transgressive, inudator regressive and emersive formations. The developmental conditions of the sedimentary reservoirs studied indicated that it would be necessary to add to them differential (according to the terminology of S. N. Bubnov), and inversive (according to the terminology of V. V. Belousov) formations which reflect the transitional stages in the development of a reservoirs. The climatic characteristics of a formation are given in accordance with the climatic constructs of N. M. Strakhov (arid, humid, etc.). Thus, formations have a dual denomination which will now be shown in describing the structure of the Precaspian reservoir.

The introduction of similar large tectonic and climatic divisions, which occupy the whole area and a large part of the sedimentary reservoir cross section, enables one to obtain information on the reservoir and on the whole historically developing system. The hierarchical structure of this system contains the intermediate developmental forms which have been fixed in the shape of the formation and in the paleoreservoirs.

The Precaspian depression is one of the largest sedimentary reservoirs on the earth. Within its boundaries sedimentary rocks have accumulated to a thickness of 20 km. The characteristic property of the geological structure of the reservoir is the widespread development of salt domes.

A systems structural study enables one to find in the Precaspian sedimentary reservoir lower Paleozoic—middle Devonian, upper Devonian—upper Carboniferous, lower Permian—Triassic, and Jurassic-Kainozoic structural formation levels, and the paleoreservoirs which correspond to them. The most detailed characteristics are of the upper Devonian—upper Carboniferous, and lower Permian—Triassic levels. It is with these that the best prospects of the oil and gas reservoirs are associated.

The arid transgressive formations of the upper Devonian initiated a new Paleozoic—Mesozoic cycle in the development of the Precaspian sedimentary reservoir. At this time the Precaspian depression experienced an intense sinking which led to the formation of a deep water basin in the depressed sediments [14].

The upper Devonian sedimentation of the eastern section of the depression formed in the coastal region of the sea basin. This is evidenced by the lithological composition of the rocks and the fauna foraminifera.

In the early and middle Carboniferous period the eastern section of the Precaspian reservoir underwent an intense sagging. In this period mainly carbon deposits accumulated which were incorporated into a humid inudator formation. Terrigenous rocks also played an important role in the structure of the lower and middle Carboniferous deposits. The composition and morphology of the sporophyte—pollen complex indicates that there was a change in the arid climate, which existed in the Devonian period, to a humid climate.

The humid inudator formation of the lower and middle carbon, which formed at a single paleoreservoir under monotypic climatic and tectonic conditions, divided into various sedimentary complexes depending on the paleogeographic

sedimentary setting. The development of primarily terrigenous sedimentary bodies in the southeastern section of the reservoir can be explained by the transfer of surrounding material into this region from the south Ustyurt mountain range, and from the end of the early to the beginning of the middle Carboniferous, from the South Embensk fold zone [5].

In the eastern and northern sections of the reservoir there was an accumulation of carbonate sedimentary bodies. In accordance with the paleogeographical setting of the sedimentary deposition, the humid inudator formation of the lower and middle Carboniferous was divided into a terrigenous complex of sedimentary bodies in the southeastern section, and a carbonate CSB in the eastern and northern sections of the Precaspian reservoir.

The humid inudator formation of the upper Carboniferous is different in comparison to the lower lying complex of sedimentary bodies. The accumulation of primarily carbonate sedimentary bodies only occurs in the northern region of the Precaspian reservoir. In the southeastern and eastern regions of the reservoir a terrigenous-carbonate CSB has developed which indicates that there was a high degree differentiation of these regions due to upheavals and sinkings. Within the boundaries these regions there was an accumulation of variously composed associated sedimentary bodies.

At the end of the later Carboniferous and the beginning of the early Permian period there occurred the first mountain formation movements in the Urals. This was accompanied by a general uplifting of the adjoining regions of the Precaspian reservoir.

The humid regressive formation of the lower Permian corresponds to the beginning of a new stage in the development of the Precaspian sedimentary reservoir. In the Preagraian period a significant part of the carboniferous deposit was eroded due to the mountain forming processes encompassing the Urals, and due to upheavals affecting the eastern regions of the reservoir. The intense erosion varied and depended on the mobility of the various beds. The formation has a roughly clastic composition in the eastern and southeastern regions of the reservoir. In the northern region of the reservoir conditions were maintained for the accumulation of carbonate sediments. In this context, the eastern and southeastern regions of the reservoir contain terrigenous CSB, and the northern region contains carbonate CSB.

Within the boundaries of the Precaspian reservoir during the Kungur period singular conditions of sedimentary deposition were established which led to the formation of an arid regressive formation. The formation of large salt sedimentary bodies became possible due to the establishment of arid conditions for sedimentary deposition, to a decrease in the tectonic activity in the Urals, and to a high accumulation rate of salt rocks. In this period, according to the data of A. L. Yanshin [13], there was a single saltlike reservoir within the boundaries of the Precaspian depression.

In the later Permian period the emersive phase in the development of the Precaspian reservoir began. As a result of mountain formation movements there was a sharp increase in the amount of surrounding material brought in from the Urals. The accumulation of sediments often occurs at a rate higher than the level of erosion. In the later Tartar period the eastern region of the Precaspian depression was raised and became a vast alluvial plain.

At the boundary of the Paleozoic and Mesozoic there was a change in the climatic conditions and, the final stage in the Hercynian mountain forming movements in the Urals was occurring [9]. These developments led to an interruption in the sedimentary accumulation, and to an increase in the processes of mechanical erosion in the removal region. All of this had an effect on the formation of the Triassic deposits. The roughly clastic terrigenous formations of the lower Triassic should belong to the emersive stage in the development of the reservoir. Middle Triassic depositions can not be found in the majority of Precaspian regions. This is the period of maximum uplifting of the region. The upper Triassic depositions are united in the humid inudator formation.

From the lower Jurassic begins a new Mesozoic Kainozoic cycle of sedimentary deposition. The Mesozoic Kainozoic depositions are transgressive regressive formations of an overall thickness greater than 1300 m.

Systems structural and systems historical investigations enable one to establish the history of the geological development of the Precaspian sedimentary reservoir. They also enable one to determine the compositions and structures occurring in the Devonian-upper Carboniferous and in the lower Permian Triassic levels.

The second stage of the lithogenetic analysis includes a systems lithological and systems functional study. The goal of this study is to obtain a generalization and systemization of results on the rock collectors and rock fluid detainers, clarify the conditions which led to the collecting and screening properties of the rocks, and to establish the laws governing the distribution of oil and gas basins over the cross section of the reservoir.

In light of the fact that the task of this paper is to point out the possibility of using the systems approach when carrying out lithological investigations, it seems appropriate to give results obtained using traditional methods for studying collector and fluid detainer rocks. A work published earlier [6] is worthy of mention. It should only be pointed out that in carrying out and generalizing the results of this study, the basic principles of the systems approach have been used. Thus,

for example, collector and fluid detainer rocks are viewed as a wholistic natural system; the basic developments of the systems functional analysis enables one to build a model of the system "clastic collector," which takes into consideration the interaction of the elements of the system and is presented in the form of a stationary operator convenient for programming [7]. In order to classify the clastic collector rocks a diagram was chosen which would enable one to present the collector and its component parts (clastic and cementing components) simultaneously as both a system, and as the elements of this system. This, in turn, makes it possible to view and study them both in tight association, and separately, independently from each other. The basic assumptions of sedimentary translation act as the theoretical basis of many of these constructs.

SYSTEMS STRUCTURAL BASIS OF PALEOGEOLOGICAL ZONING

A structural–lithological typification of sedimentary reservoirs [7] and the carrying out of a systems structural and systems historical study enables one to establish new principles governing oil and gas geological zoning. It also enables one to develop a method of geological and geophysical study to be applied to sedimentary reservoirs and to choose the optimum direction for carrying out oil and gas exploratory work.

Geological zoning is the basis for predicting the location of oil and gas deposits. It involves isolating perspective oil and gas containing elements and deposits within the boundaries of the earth crust under study.

Much attention is given to the development of the geological zoning of large-scale oil and gas territories and aquatories. In this context investigators use various approaches in delineating and classifying oil and gas regions. I. O. Brod, A. A. Geodekyan, N. A. Eremenko, A. A. Trofimuk, V. E. Khain, and others consider the oil and gas reservoir (OGR) as the basic unit of geological zoning. A. A. Bakirov, E. A. Bakirov, G. E. Ryabukhin, Z. A. Tabasaranskii, G. T. Yudin, and others consider the basic element of geological zoning to be the oil and gas region or province.

I. O. Brod et al. [3], in delineating OGR, exclude from their classification large absolute structures, which, according to the authors, act as buried structural boundaries between two neighboring reservoirs. They allow for the fact, however, that oil and gas deposits can often be coordinated with such buried barriers. Examples given are sites associated with the Mesozoic deposits of the Caspian terrace which separate the Middle Caspian reservoir from the North Caspian; sites associated with the Paleogene deposits of the Stavropol outcrop which divide the Middle Caspian and Azov–Kuban reservoirs, and the multiple and rich stores of oil of the Tsintsinnat anticline which divide the Michigan and Illinois reservoirs from the Appalachian; and deposit sites associated with the Bend anticline which divide the Permian reservoir from the Mexican Gulf reservoir.

A. A. Bakirov [1] pointed out that the concept of an oil and gas reservoir did not include all of the various geostructural elements of the earth's crust, and that often the most highly productive interreservoir upheavals "fall out" of its limits.

The delineation of oil and gas provinces and regions can also be criticized due to a lack of a sufficient historical and genetic basis for sections of the earth's crust which have been isolated during zoning.

A transition to paleogeological zoning enables one to overcome the deficiencies of the traditional approaches to oil and gas geological zoning. At the very least, the structural formation levels delineated by systems structural studies and the paleoreservoirs which belong to them make it possible to establish the most perspective zones of oil and gas accumulation for each large stage in the development of an area of the earth's crust under study.

In paleogeological zoning isolated objects have a sharp historical–geological and genetic basis. Highly productive deposits and upheavals (from this point on interreservoirs) are located within the boundaries of paleoreservoirs. It is within these boundaries that oil and gas accumulation and formation occurs, and a historical geological analysis of the paleoreservoir development enables one to establish the characteristics within their limits which lead to the formation of highly productive deposits and structures.

The paleoreservoir is the basic component of paleogeological zoning and is the separate object for study and subsequent oil and gas exploratory efforts. The advantage of paleozoning consists in the fact that it enables one to more clearly determine objects which can be explored for hydrocarbon accumulations.

The nature of tectonic movements predetermines the positioning of sedimentation reservoirs, regions of upheaval, the nature of coastal lines, and so forth. Therefore, the first stage in understanding comes after a study of the overall direction of vertical oscillatory movements and the extent of this movement over definite geological periods of time. The

hierarchical structure of the "sedimentary reservoir" system, which fixes the evolutionary stage of the reservoir as a whole developing system, shows that paleoreservoirs are a unique landmark in this development. The establishment of laws governing the distribution of paleoreservoirs and their evolution facilitates understanding, on the one hand, of the geological history behind the development of the reservoir, and on the other, of the laws governing the distribution of oil and gas accumulations.

A schematic picture of the Precaspian reservoir has been constructed which illustrates the thickness of variously sized deposits, and, consequently, the distribution and evolution of sedimentary reservoirs.

An analysis of the schematic and structural pictures developed leads to the conclusion that the eastern part of the Precaspian reservoir was an area of variously directed movements in the Paleozoic period. This area affected to various degrees the local substructures. Up to the end of the middle and beginning of the later Devonian there were many general characteristics in common. with the development of the remaining regions of the eastern European bed [5]. Transgressions of the late Devonian caused an intense bending of the central region of the Precaspian paleoreservoir [14]. As the completed construct shows, the maximum thickness of the sediments of the Devonian—Artinskian age exceeded 4000 m, and belonged to areas which were located close to the central region of the depression. In the eastern regions the thickness of these deposits was 500 m less.

In the early and middle Carboniferous period a more intense accumulation of sediments occurred in the eastern regions of the paleoreservoir. Here deposits accumulated which were 300-500-m larger than those areas located in the central region of the paleoreservoir. At the end of the later Carboniferous to the beginning of the early Permian period mountain forming processes were occurring in the Urals, and the maximum region of sedimentation again shifted to the western area of the territory and their thickness increased by 300-350 m.

Despite the fact that erosion of the accumulated sediments occurred, which makes the reconstruction difficult, all of the remaining signs point to the fact that there was a shift in the regions of maximum sedimentation (from the western to the eastern and again to the western). From this one can conclude that the mobility of the substructure played an important role in the historical development of the territory under study. The mobility of the eastern and western regions was the greatest. Between these two regions were located one or several relatively stable areas. The mobility of the various substructures could not but have an effect on the processes of oil and gas formation and accumulation. As an analysis of the oil and gas formations shows that all of them, including working deposits, belong to the eastern region slope, and within its limits, to the slope of the substructure outcrops which formed in the regions of stable submersion. Thus, the Kenkiyan deposit is associated with the southern slopes of the Enbek substructural outcrop. It belongs to a local subsalt upheaval located within the limits of active sedimentation which existed here over the whole Paleozoic period.

Also studied are the characteristic placements and evolution of the paleoreservoirs of the Siberian bed. Schematics were constructed describing the locations of paleoreservoirs for the middle and late Proterozoic, Cambrian and Ordovician, Silurian and Devonian, Carboniferous and Permian, and Mesozoic whose deposits are divided by regional nonconformities and which form structural and formational levels. These schematics enable one to follow the development of the Siberian bed, to establish the types of large-scale geological elements present, and to determine their associations with oil and gas accumulations [6].

The currently discovered and working deposits of oil and gas in the territory of the Siberian bed are mainly associated with: the anticlinal sections of the large paleoupheavals of the late Proterozoic—early Paleozoic period and to their slopes which are directly adjacent to the vast paleosynclises and paleodepressions which have undergone extensive sagging;

the borders of large paleosynclises of the late Proterozoic and early Paleozoic periods which are characterized by a significant amount of oscillation;

and with the regional depressions of the late Paleozoic and Mesozoic periods.

A GEOLOGICAL AND GEOPHYSICAL METHOD TO STUDY SEDIMENTARY RESERVOIRS

In a systems analysis sedimentary reservoirs are viewed as historically developing natural systems. The delineation of elements and subsystems at different levels in a hierarchy (natural reservoirs, oil and gas complexes, structural and

formational levels, or sedimentary paleoreservoirs) enables one to detail the investigative process and to establish the nature of its oil and gas content.

In the systems approach the method of regional geological and geophysical examination is based on a study of sedimentary reservoirs as wholistic natural systems. This enables one to obtain information on the structure of the reservoirs as a whole, to discover the main zones of oil and gas accumulation, and to develop an optimized exploration program.

It is recommended that the regional studies be carried out in several stages. The work in the first stage should be carried out based on the characteristic structure of the sedimentary reservoir. This structure consists of either symmetrical or asymmetrical formations which differ in stratum size and thickness.

In the development of the reservoir there is a migration zone of maximum thickness in space and time, and there is a change in the boundaries of the reservoir. As a rule, at the borders of its sections there is a thinning of the surrounding collector stratum and shift of the rocks in the lateral direction. Such structural characteristics provide a basis for recommending, even at the first stage of the study, that one concentrate the regional geological and geophysical investigations along radial directions from the reservoir borders towards its central area, and for smaller reservoirs investigation should proceed along the diameters [6]. This would enable one to study the structure of sedimentary reservoirs as a whole, to uncover the most prospective oil and containing ones, to determine their boundaries and sizes, and to establish zones of maximum sedimentary accumulation.

The establishment of possible oil and gas containing zones is the main task of the second stage of the regional geological and geophysical investigation.

In studying sedimentary reservoirs of the Precaspian type, which are characteristically large, of significant sedimentary thickness, and are manifestations of salt tectonics, it is recommended that one carry out the study along radial directions. This makes it possible to study the structure of separate areas of the substructure which, as a rule, are submerged from the borders of the reservoir to its center in steps. It also allows one to specify the structures of large tectonic elements associated with substructural areas, to study neighboring geotectonic elements cojoined to the reservoir, to establish the presence or absence of large shelf bodies which may be coordinated with border regions of the bench, and to establish the structure of the natural reservoirs, oil and gas complexes, and the oil and gas producing potential of the deposit.

The development of AVPD in the subsalt deposits of Precaspian type reservoirs prevents the densification of the surrounding rock. This allows them to maintain sedimentation capacities down to depths of 5-6 km. In carbonaceous rocks the formation of secondary capacity is widely developed. This is noticed down to a depth which exceeds 5 km. This is necessary to take into consideration when planning exploratory work.

In Vilyuisk type reservoirs the precise description of the tectonic structure of the reservoirs is one of the main tasks, as well as establishing their location, defining the boundary regions, and studying areas of regional thinning which are adjacent to the boundaries. Due to the fact that there are sharp changes in volcanic-sedimentary bodies, one must carry out more detailed studies in order to obtain information on the structures of natural reservoirs and oil and gas complexes. When large positive tectonic elements are located in the central regions of reservoirs which have been sufficiently studied (as, for example, in the Vilyuisk syncline), it is recommended that one carry out regional second stage studies along radial directions from congruent upheavals to the boundaries of the reservoir.

In carrying out second stage studies it is necessary to orientate the geological and geophysical investigations in accordance with the sedimentary capacity depth of the surrounding collectors. In apsheronk type reservoirs rocks with good collector characteristics can be found to a depth of 6-7 km, and in Preural-type reservoirs they can be found down to a depth of 2-3 km. In this context when studying the latter it is necessary to concentrate on the carbonaceous rocks as the more favorable type of rock in which conditions for the development of secondary capacities are maintained at greater depths.

Third stage regional work should be concentrated on the study of structural formation levels or sedimentary paleoreservoirs, and on the more perspective sections such as the central areas and the slopes of large geostructural elements. Other areas in this category include regions of large positive neighboring structures and zones in which there are large accumulations of sediments, boundary regions of the paleoreservoir, and positive upheavals in the central area of the paleoreservoirs.

The delineation of paleoreservoirs as unique objects for the discovery of oil and gas enables one to give their recommendations for the most optimum exploratory work. It also enables one to rapidly and inexpensively discover accumulations of migrating hydrocarbons which are associated with various geostructural elements.

Irrespective of the fact that the majority of sedimentary reservoirs in the former soviet union have been fairly well studied, one should not believe that the first stage of work has been completed. The carrying out of studies which provide information on the overall structure of sedimentary reservoirs could lead to new interpretations of the results given by former geological and geophysical studies.

Work that has been carried out has shown that geological systems studies provide a number of methods which enable one to obtain additional information concerning the structure and oil and gas content of sedimentary reservoirs.

The use of the systems approach points out the necessity of further improvements in the traditional methods of geological investigation, and the creation of effective methods for development of resources in new oil and gas containing regions.

Thus, a systems lithogenetic analysis, which includes systems structural, systems historical, systems lithological and systems functional studies, enables one to view sedimentary reservoirs as historically developing systems, and to develop a means for effectively predicting the location of oil and gas containing regions. It also enables one to establish new principles of oil and gas zoning, to develop a method of geological and geophysical study of sedimentary reservoirs which views them as wholistic natural systems, and to choose the optimum direction for oil and gas exploratory work.

* * *

A renewed interest toward the material composition of rocks plays an important role in the development of the geological sciences. At the same time, disconnected data exists in the lithological literature which is not being effectively used in the closely related geological disciplines.

Lithology has over the course of its development been well-prepared for the incorporation of the systems approach. The traditional systems structural and systems functional studies in a systems analysis can be effectively used in lithology. The carrying out of such studies in combination with a systems historical approach would enable one to increase the effectiveness of the historical genetic and comparative lithological methods. It would also reflect the specifics of geological objects which have developed as wholistic natural systems.

The systems approach makes it possible to develop multiple and variously scaled studies, and quantitative and qualitative methods which enable one to obtain a maximum amount of information from the lithological studies, and to understand them at a new level of generalization of the factual material.

For an effective use of the systems approach it is necessary to continue work aimed at the development of a methodological and theoretical foundation for geological systems studies. Much attention should be given to the development of the corresponding methodological conceptions, and also to an understanding of the principles and methods of the systems approach in geology. The success of systems studies will depend to a significant degree on the development of a theoretical basis for systems structural, systems functional, and systems historical investigations, on the development of a rational combination of form and content methods, and on the development of qualitative methods for the study of geological systems. The solution of these problems would increase the effectiveness of the systems approach as applied to geological science and practice.

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METAL SOURCES OF RECENT Fe–Mn ORE MINERALIZATION IN PELAGIC OCEAN AREAS. PART 1. MANGANESE.

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UDC 550.4:553.31 + 32

The current Mn distribution patterns in oceans and the Fe–Mn ore mineralization processes in the pelagic zones are linked to terrigenous (volcanic–terrigenous) sources of these elements. The hydrothermal Mn supply is less important and represents 0.5 million tons/yr. A striking increase in the role of hydrothermal Mn-flux rate to pelagic deposits, reaching the level of terrigenous influx, would radically change assumptions on the mechanism of oceanic sedimentation.

Questions, concerning the source of elements that form Fe–Mn concretions and crusts in pelagic areas of the World Ocean have not yet been resolved. Two genetic theories (a volcanogenic and a terrigenous) were presented [36] immediately after the discovery of this pelagic ocean floor phenomenon. Quite detailed up-to-date discussions on the problem occur in two publications [3, 19]. Most authors, except those who advocate extreme ideas, believe that the ore process was active in all pelagic sediment and ore formations. Extreme views also exist. For instance, Strakhov considered the terrigenous flux dominant; from volcanic sources providing but a few percentages of the ore metal content [32]. I calculated the volume of sedimentary Mn that occurs in the ocean and its pelagic sediments, comparing it with hydrothermal supply from rift zones of the seafloor. Calculations have indicated that, the total hydrothermal Mn on the seafloor is c. 3% of the total. In pelagic sediments, the Mn content reaches 8% [9]. In addition, several calculations by Lisitsyn indicated the dominance of hydrothermal over terrigenous sources in the pelagic ocean zone. In his view, hydrothermal Mn provides 70–80% of the Mn content in pelagic sediments [23–25].

One agrees with Mero [28, p.20]: "any exhaustive theory on Mn concretion genesis must include an explanation for the presence of all participating elements." However, data are scant on other ore elements. Hydrothermal flux calculations provide low figures. Lisitsyn [24], based on another work [5], estimates 30% Fe, 29% Co and 10.4% Cu hydrothermal components in Pacific pelagic sediments.

The question of the element source is crucial in solving this problem and in establishing a genetic theory of oceanic Fe–Mn ore development. This work uses recent data, based on quantitative estimates on the terrigenous and volcanogenic (hydrothermal) flux to the ocean, the geochemistry of sediment and ore matter, and the geochemistry of sediments and concretions (crusts) in the ocean. An attempt is made to resolve the question of metal sources, including ore element source in Fe–Mn concretions. By the examples of Mn, Fe, Cu, Ni, Co, and Zn, this issue is being discussed in a series of three future publications.

MANGANESE SUPPLY TO THE OCEAN

In searching for sources of manganese that enter the ocean the role of continental rocks that participate in the solid and dissolved sediment stream flux is vital. This search also involves eolian, glacial and abrasional matter; volcanoclastic-matter of basalt-andesite composition; hydrothermal flux, essentially from the axial zones of oceanic rift zones and, to a certain extent from transform fractures and underwater volcanoes. In contrast with terrigenous and volcanoclastic matter that enters pelagic ocean areas mainly through the near-continental zone of deposition, the hydrothermal flux of dissolved Mn to the ocean pelagic zone is almost entirely direct in nature. With rare exceptions, it is essentially pelagic.

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Annual sedimentary Mn flux to the ocean is estimated by Mn concentration values. Mn is calculated in the total solid and dissolved flux. Table 1 and additional data [31, 21] on sediment supply to the ocean provides the basis. Different values resulted from different estimates on river suspendates: 12.7 billion tons/yr, according to Strakhov and 18.5 billion tons/yr, according to Lisitsyn. Vasil'ev's [6] data were accepted for Mn in solid river discharge. This work contained significantly more information on the mean multiyear discharge of 436 rivers, calculated for river mouth areas. A new extensive database was obtained on solid sediment flux, including in particular, the first calculated data on stream bedload. The final calculation of the total solid stream discharge [6] provides 19.3 billion tons/yr. 16.3 of this is stream suspendate, represented generally by aleurolitic-pelitic matter. 3 billion tons/yr (or 18.4% of the suspendate) was bedload that consists of sandy-gravelly size varieties. Strakhov [31] estimated the bedload ratio as 10% (1.3 billion tons/yr). In addition, the pyroclastic supply (c. 2-3 billion tons/yr) was not calculated precisely. Stream water flux to the ocean was taken as 43,000 km³/yr [1]. Groundwater flow, based on [16], was calculated 2200-2400 km³/yr (about 5% of the surface flow) and was omitted from Mn balance calculations.

Thus, the yearly sediment flux figures to the ocean (21.5-27.8 billion tons; Table 1), were used as possible minimum and maximum values. The corresponding range of nonbiogenic sediment matter was 19.6-25.9 billion tons.

The range of sediment volume that annually enters the ocean should not be considered noncalculable. Maximum estimated solid stream sediment flux [6] appears to conform with actual conditions. Strakhov's [31] minimum figure assists in defining a trend that ended with the start of the anthropogenic-agricultural era on our planet. Obviously, the start of agriculture, mining and industrial surface denudation resulted in gradual increase of sediment transport via streams and eolian transit to the ocean. Exact calculations of global human impact are unavailable.

The mean Mn content in stream suspendates and solutions is 0.11%, respectively, 10 µg/liter [12, 14]. In non-differentiated matter, the stream bedload, coarser than sand, is estimated to have a Mn content that corresponds to the Mn clarke value in sedimentary rocks. A wide range characterizes Mn in eolian sediments [22], between few hundredths to a few tenths of one percent. This paper adopts the 0.07% figure. Baturin [3] indicated that the mean Mn content in eolian matter is 0.05%. The Mn content in glacial sediments and products of shore abrasion, was similarly accepted as 0.07%. This is the mean value for sedimentary rocks [7].

In andesites the Mn clarke is 0.11% [7]. According to different authors, various basalt types contain 0.12-0.2% Mn. Therefore, 0.12% Mn was accepted as mean value for volcanoclastic matter.

Calculations (Table 1) indicated that 20.2-26.5 million tons Mn/yr settles in the ocean. Most of the Mn enters as solid terrigenous and volcanoclastic matter. Solutions play a negligible role (0.43 million tons, or 1.5-2.0%). Apparently, terrigenous matter predominates in the sediment matter. Volcanoclastic Mn represents only 12-14% of the total. Table 1 shows stream suspendates as the prime Mn source; they represent a maximum 70% of the total flux to the ocean.

Estimates of the total annual hydrothermal Mn supply to the ocean (Table 2) differ by more than one magnitude order [3]. Hydrothermal sources, according to various workers introduce 0.5-10 million tons Mn/yr to the pelagic ocean zone. Subsequent calculations [37] that supplement data in Table 2 indicate that hot hydrotherms at 21°N, East Pacific Rise, and the Galapagos spreading center introduce 2.8-8.8 million tons Mn to the ocean. Calculated buried hydrothermal Mn volumes in metal-bearing sediments of the East Pacific Rise must also be considered. 0.175 million tons/yr of the hydrothermal Mn was estimated to accumulate in 10 million km² of metal-bearing southeast Pacific Ocean floor deposits adjacent to the East Pacific Rise [5]. Metal-bearing deposits are less widespread in the Atlantic and Indian Oceans. One may assume that Mn from hydrothermal sources is much more widespread on the seafloor and reaches well beyond the area of metal-bearing sediments. This would triple the Mn values, assuming that the ocean bottom sediments would be receiving c. 0.5 million tons Mn/yr. This value corresponds to the minimum value in Table 2. The data reflect the fact that presently no reliable calculations exist on the hydrothermal component of the Mn flux.

Comparison of the maximum figure (10 million tons) of hydrothermally introduced Mn to the ocean, with Table 1 indicates that the total oceanic hydrothermal production at most represents one-third to one-fourth of the total Mn volume.

Mn BURIAL IN OCEAN SEDIMENTS

Distribution of sedimentary matter on the ocean floor conforms with the overall pattern of oceanic sedimentation. According to Lisitsyn [22, 23], 1.73 billion tons of nonbiogenic sediment settles annually from the pelagic ocean below 3000 m depth. This depth practically coincides with the ocean floor area. The rest of the sediment matter settles in the ocean bottom margin along the continents that includes river mouths, continental shelf and slope, slope-toe areas. Sediment

accumulation rates (Table 1) range between 17.9-24.2 billion tons/yr. The area of near-continental deposition corresponds to the area of avalanche sedimentation. From this transitional zone does the pelagic ocean receives its finest sediment fractions.

The depositional conditions are most varied, both in the pelagic and near-continental zones. Many open ocean shelf areas are totally devoid of unconsolidated sediments. This also is the case in steep continental slope areas. Extremely high sedimentation rates occur with deposition of huge sediment volumes on shelves, river mouth regions near numerous large streams, over continental slope toes, and on continental slopes. Deposition rates are uneven in pelagic areas. Differences may amount to 100 times or more, according to measurements in the pelagic zone. Charts show a range between mean rates in the pelagic zone; from 0.05 g/cm² in central areas of deep-water basins, to 0.5-2 g/cm²/1000 yrs in the pelagic rim [22]. The Fe-Mn concretion ore zone is represented by <0.2 g/cm²/1000 yrs rates. Significant amounts of Fe-Mn concretions also occur in areas with 0.2-0.5 g/cm²/1 ka deposition rates.

Presently, oceanic ore field areas are poorly defined [2, 19]. Baturin [3] estimates their total as c.47-50 million km², corresponding to 17-18% of the total pelagic ocean.

Based on Mn burial in ocean deposits and indicated variations in sediment accumulation, including the known Mn distribution patterns, our three-zone model includes the area of near-continental sediment accumulation, and the pelagic area of deposition, including the Fe-Mn concretion fields. Figure 1 provides a schematic outline of the model. In near-continental depositional areas Mn originates exclusively from sedimentary sources. A hydrothermal Mn source is also important in the pelagic belt.

Sedimentary Mn Distribution between Major Depositional Areas. A large Mn concentration database in central and marginal seas (Black, Baltic, Bering, Okhotsk, Japan, etc.) and in sediments of shelves, continental slopes and slope toe, deep ocean trenches along the Pacific, Indian ocean and Atlantic margins, indicated 0.02-0.09% Mn content in terms of the total nonbiogenic matter.* The exact mean Mn content was 0.056%. Data were derived from near-continental sediments. The sediments differ in compositional-genetic characteristics (terrigenous, volcanic, and biogenic-terrigenous types) but have one common feature. Due to diagenetic processes involving high organic matter content, the deposits are reducing. Even in the sediment surface Mn often is exclusively bivalent. Mn is always bivalent within the sediment bed beneath an oxidized film of varying thickness.

Figure 2 shows Mn distribution in a sediment profile near Japan, northwestern Pacific. The profile extends from the shelf at the islands of Japan (Sangar Bay) to the central Northwestern Trench [10, 27, 34]. Starting from Shelf Station 6159 (Fig. 2), the weighted mean of Mn in the core remains low (0.06-0.07%) in the open ocean nearshore and hemipelagic sediments (Zones I and II). This value rises quickly only in an area of transitional clayey muds (Zone III). In the transition toward oceanic deep pelagic red clays (Zones IVA and IVB), with the Fe-Mn concretion ore zone in the profile, the Mn content remains high. Concentrations here are 7-8-times greater than in nearshore deposits (Zone I). Mn-enrichment of the surface layer in the hemipelagic zone (Zone II) did not alter the weighted mean Mn values (Fig. 2). Low Mn concentrations, therefore, are typical not only of nearshore shelf sediments, but also of the continental slope and its toe (Station 6163, Japan Trench). Sediments with low Mn values extend far into the ocean and include hemipelagic ocean floor deposits. The Mn distribution pattern in the Japan profile is typical of the ocean. This is shown by published data from the California and Peru profiles in the Pacific, and in Indian and Atlantic ocean sediments.

The last calculations deal with the higher mean Mn values in sediments in near-continental areas of the ocean. They represent an increase by 15-20%. This concentration was the source for the 0.07% mean value for continental sedimentary rocks [7]. Increased Mn concentrations occur in anaerobic marine, especially basin, deposits in certain instances (e.g., Gotland and Landsort Basins, Baltic Sea; Farallon Basin, Gulf of California; in hydrogen sulfide-saturated Black Sea waters). In addition, continental sedimentary rocks are analogous to recent marine and marginal ocean sediments. Examples of deep water sandy ocean deposits are unknown from continents.

By using the mean (0.07%) Mn concentration in deposits of near-continental ocean zones, these values appear as transitional between near-continental and pelagic regions, the two main areas of deposition (Table 3).

Table 3 shows that in the near-continental area the sedimentation rate is 30-40-times greater than in the pelagic belt (20-27 and 0.63 g/cm², correspondingly).

*Data refer to weighted mean Mn concentrations in sediment cores from the seafloor.

TABLE 1. Yearly Mn Supply to the Ocean in the Sediment Cycle

Substance and source	Weight, billion tons	Mn percentage	Mn matter	
			million tons	%
River flow:				
suspendate	12,7-16,3	0,11	14,0-17,9	69,3-67,6
bedload	1,3-3,0	0,07	0,9-2,1	4,5-7,9
River flow (biogenic sedimentation; CaCO ₃ and SiO ₂)	1,9	—	—	—
Eolian matter, matter from shore erosion and ice	3,6	0,07	2,5	12,3-9,4
Volcanoclastic matter (andesites, basalts)	2,0-3,0	0,12	2,4-3,6	11,9-13,6
Mn in river water solutions	43000 km ³	10 microgram/liter	0,4	2,0-1,5
Total	21,5-27,8		20,2-26,5	100
Nonbiogenic sediment matter	19,6-25,9			

TABLE 2. Calculated Total Hydrothermal Mn Influx into the Ocean [3]

Mn matter, million t/yr	Calculation method	Literature reference
0,7	Based on global balance of sediment accumulation	Horn, Adams, 1966
3,5	Based on Mn-supply dependence on spreading rate - $0,230 \pm SR^* \cdot 0,233$	Bostrom, 1972/1973
0,7-7,2 (mean: 1,4)	Based on geochemical balance (with certain modifications)	Elderfield, 1976
0,9	Based on hydrothermal flux	Lyle, 1976; Bender et al., 1977
10	Based on Mn ³⁺ /He ratio = $4 \cdot 10^5$	Weiss, 1977
4-10	Based on Mn/heat flow value = $(1,5-3,9) \cdot 10^9$	Corliss et al., 1979
0,51	Based on underwater basalt weathering	Staudigel, Hart, 1983
1,6-1,9	Based on the cold and hot contact of ocean water with basalts	A. P. Lisitsyn, 1983

*SR — spreading rate.

Data in Table 3 indicate that in the near-continental area where 91-93% of the sediment that enters the ocean settles, only 60% of the Mn accumulates. Annually 7.7-9.6 million tons (36-38%) of sedimentary Mn settles in the pelagic area. This involves mostly stream suspendates and volcanoclastic matter. Table 1 shows that stream water solutions transport only 0.43 million tons Mn to the ocean.

Two sources may account for Mn distribution in ocean sediments and the insufficient distribution of sediments between the near-continental and pelagic depositional zones [9]. First, the pattern may result from well-known diagenetic processes of Mn redistribution in reducing sediments. After deposition on the bottom, with conditions reducing in the sediment layer, often on its surface, Mn(IV) is reduced to Mn(II) in the sediments. It enriches the muddy water. Due to differential Mn(II)-concentration, diffusional flow enters the near-bottom water layer from the muds. As it is introduced into oxygen-rich waters, Mn(II) is oxidized to Mn(IV) and is subjected to hydrolysis. Gel- or subcolloidal particles of hydrated dioxide settle from bottom currents at locations where the presence of Mn(IV) is not inhibited by redox conditions on the bottom surface. Mn probably is subjected to several cycles of reduction-oxidation as it reaches the pelagic ocean.

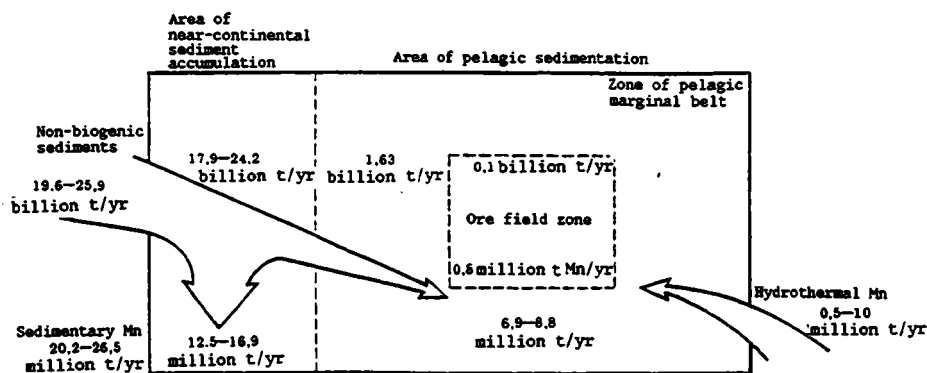


Fig. 1. Block diagram of nonbiogenic sediment and Mn influx to the ocean and their distribution pattern in major depositional areas. Hydrothermal sources supply Mn only to pelagic depositional areas.

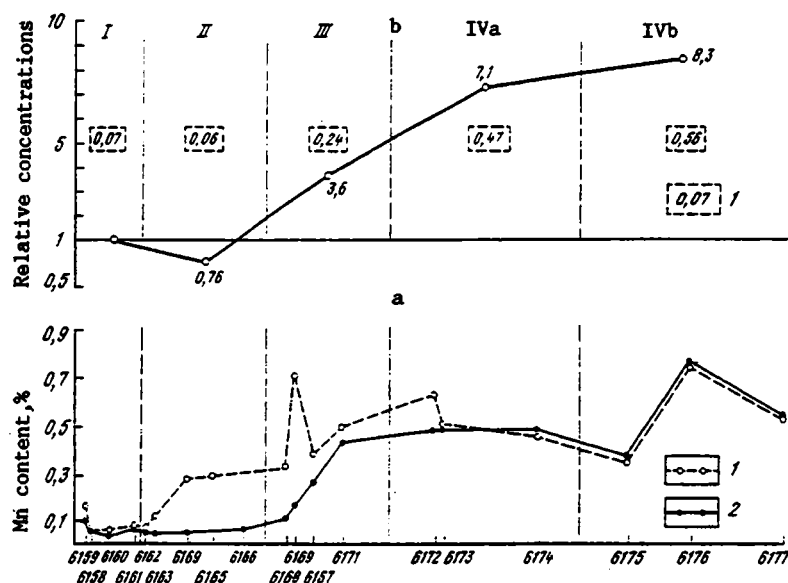


Fig. 2. Mn distribution in Pacific ocean deposits in a profile between the Japan shore and the central Northwest Basin. I-IV) compositional-genetic sediment categories: I) nearshore; II) hemipelagic; III) transitional clays; IVa) pelagic clays with volcanic ash layers; IVb) pelagic clays with zeolites. a) Mn (in % of dry matter) in surface sediment layer (1) and weighted mean in core (2); b) relative Mn concentration in sediments of profile (weighted mean value in nearshore deposits, taken as unity). Framed figures: weighted mean values for each zone.

According to Baturin [3], the maximum potential Mn flux equals 4.35 million tons annually. Maximum 30% of the original Mn content may be lost from the terrigenous matter due to reworking under reducing diagenetic conditions.

Second, Mn-enrichment of sediments in the pelagic ocean may be explained by the absence of settling of colloidal/subcolloidal suspensates that are most enriched in the Mn-fraction of river suspensates. This happens in the area of avalanche deposition at the river—sea interface. The suspensate enters the oceanic sediment cycle and spreads sedimentary matter in the pelagic zone. This mechanism includes recurring ingestion of fine suspensates by the biota and segregation, through biofiltration, of dissolved Mn into nonorganic and organic Mn(II)-compounds. This process follows oxidation and hydrolysis, with precipitation of hydrothermal Mn(IV)-dioxide and repeated introduction of fine suspensates to ocean currents. The currents then distribute this matter throughout pelagic ocean areas.

TABLE 3. Distribution Pattern of Sedimentary Mn Concentrations in Major Areas of Sediment Accumulation

Sedimentation zone	Area		Amount of nonbiogenic sediments	
	million sq km	%	billion t/yr	%
Near-continental	87,6	24,3	17,9-24,2	91,2-93,3
Pelagic	272,6	75,7	1,73	6,7-8,8
Total	360,2	100,0	19,6-25,9	100,0

Sedimentation zone	Mean Mn content, in %	Mn amount	
		billion t/yr	%
Near-continental	0,07	12,5-16,9	62-64
Pelagic	0,44-0,55	7,7-9,6	36-38
Total	0,103	20,2-26,5	100,0

TABLE 4. Distribution of Sedimentary Mn on Ocean Floor (total Mn supply: 20.2-26.5 million ton/yr)

Parameters	Total (mean)	Depositional areas and types of Mn burial					
		near conti- nental (un- consol- idated sedi- ments	pelagic				
			total (sedi- ments and Fe- Mn con- cre- tions)	peri- phery of pella- gic areas	ore field		
					total (sedi- ments and Fe- Mn)	uncon- solidated sedi- ments	Fe-Mn concre- tions
Ocean area, million sq km	360,2	87,6	272,6	222,6	50	-	-
Total sediment amount, t/yr	21,5-27,8	18,5-24,8	3,0	-	-	-	-
Amount of nonbiogenic sediments, billion t/yr	19,6-25,9	17,9-24,2	1,73	1,63	0,1	-	-
Mean accumulation rate of nonbiogenic sedi- ments, g/sq cm/thousand yrs	5,4-7,2	20-28	~0,6	~0,9	0,2	-	-
Mean Mn content, in %	0,103	0,07	0,44-0,55	0,4	-	0,8	20
Total Mn content, million t/yr	20,2-26,5	12,5-16,9	7,7-9,6	6,5	1,2-3,1	0,8	0,4-2,3
Accumulation rate of total Mn, mg/sq cm/ thousand yr	5,6-7,4	14,3-19,1	2,8-3,5	2,9	2,4-6,2	1,6	0,8-4,6
Total of Fe-Mn concre- tions, million t/yr	-	-	-	-	-	-	2,0-11,5

Our calculated figures (Table 3) of total sedimentary Mn (7.7-9.6 million tons) that annually reaches the ocean pelagic in the avalanche sedimentation zone at the stream-sea interface, approximate the values of annual Mn accumulation in the pelagic zone (8.35 million tons). They were determined from direct suspension-mixing and based on data of total volume [23-26]. Because of the similarity between figures reached independently, one notes the main difference between various interpretations, regarding the source of Mn concentrations in the pelagic ocean area.

It is clear from discussions and data (Tables 1, 3) that our Mn figures from the pelagic ocean, 7.7-9.6 million tons/yr are based on the supply of Mn by sediments (volcanoclastic-sedimentary matter) from the land. Endogenic (hydrothermal) Mn supply to the pelagic zone can not be considered. It is somewhat surprising how certain manipulations,

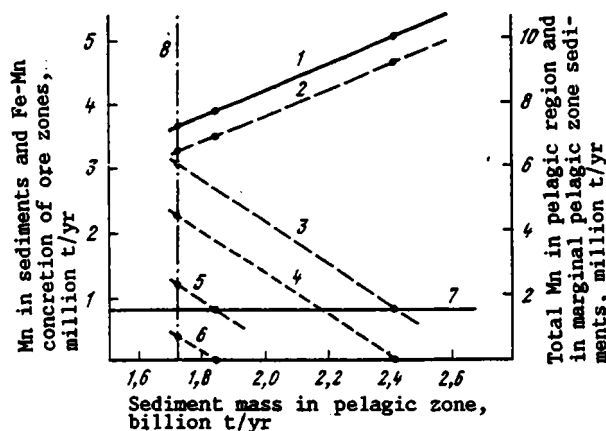


Fig. 3. Changes in total Mn amount (million ton/yr) in pelagic deposition area and in ore zone sediments, and changes in the total amount of non-biogenic sediment matter (billion ton/yr) in pelagic zone. 1-7) total amount of Mn: 1) total value in pelagic deposition area; 2) in sediments of the pelagic rim zone; 3) in unconsolidated sediments of ore belts, with deposition rate of nonbiogenic sediments in the ocean, 2569 billion tons/yr; 4) in Fe-Mn concretions, with same value of nonbiogenic sediments; 5) in loose sediments of ore zones, with nonbiogenic sediment flux of 19.6 billion tons/yr; 6) in Fe-Mn concretions with same nonbiogenic sediment flux; 7) amount of Mn (0.8% million tons/yr in loose sediments of ore zones), at 0.8% Mn content and nonbiogenic sediment flux of 100 million tons/yr; 8) amount of nonbiogenic sediments in pelagic zone, according to A. P. Lisitsyn (1.73 billion tons/yr).

multiplication of and subtraction regarding Kurnosov's ratios [20], resulted in a figure of 10.54 million tons/yr hydrothermal Mn flux, delivered to the pelagic ocean zone [9].

Lisitsyn [23] determined the total mass of Mn in oceanic pelagic sediments as 8.35 million tons/yr. Essentially, this is in agreement with data in Table 3 and indicates that 6 million tons/yr of the value is endogenic Mn. How was the hydrothermal Mn volume obtained? Based on a total Mn flux of 15.5 million tons/yr and calculating Mn loss from suspendates at the stream-sea interface as 47% (Table 4), Lisitsyn [23] notes: "direct Mn suspension, according to new charts, leads to 8.35 million tons annual Mn accumulation. Sediment from land, after passing through the estuarine barrier and losing 53% of the suspended and 70% of dissolved Mn load of the original stream content, amounts to 1.6-2 million tons total Mn. The difference, 6 million tons, is assigned to endogenic sources" [23]. Disregarding the omission (a loss of 47%; not 53% of the suspended Mn), it is unclear how the 1.6-2 million tons figure came about in calculating Mn loss from land to the pelagic zone. $15.5 \times 0.53 = 8.2$. The figure would indicate that Mn crosses the river-sea barrier and annually 8.2 million tons settles directly in the pelagic zone. This value is in perfect agreement with Lisitsyn's figure of 8.35. The figure shows that endogenic Mn plays no role in the pelagic zone.

Publications [26] more recently have claimed that 11 million tons/yr Mn, or 52% of the 21 million tons total stream sediment flux in the stream-ocean mixing zone, enters the ocean. According to Gordeev [12], 12.8 million tons of 20.8 million tons/yr total Mn in the mixing zone reaches the ocean. Thus, the total Mn loss at the river-sea interface is 38%. Only 62% settles in the ocean. Clearly, this Mn ratio involves only stream suspendates, not solutions. Nevertheless, according to Lisitsyn, "the suspendate flux of these elements (including Mn - I.V.) plays almost no role in pelagic sedimentation [24, p. 66]. A generalized discussion on Mn geochemistry in the ocean states that 70-90% of river suspendate, including the Mn suspendate settles at the river-sea geochemical interface [25, p.4]. This view is stated even more categorically on the following page: "maximum 90% Mn of stream suspendates and 20-60% of the soluble Mn in stream waters settles at the stream-sea interface".

TABLE 5. Distribution of Sedimentary Mn on Ocean Floor (minimum influx of river suspendates, with maximum possible concentration of pelagic sediments. Very low level of Fe—Mn concretion development)

Parameters	Total (mean)	Mn sedimentation areas and burial types				
		near con- tinental (uncon- solidated sediments)	pelagic zone			
			total (sedi- ments and Fe-Mn concre- tions)	periphery (uncon- solidated sedi- ments)	ore zones	
					unconsol. sediments	Fe-Mn con- cretions
Area, million sq. km	360,2	87,6	272,6	222,6	50	-
Total sediments, billion t/yr	20,5*-27,8	17,5-24,2	3,0-3,6	-	-	-
Amount of non- biogenic sedi- ments	18,6*-25,9	16,9-23,5	1,7-2,4	1,6-2,3	0,1	-
Mean rate of nonbiogenic sedimentation, g/sq cm/1000 yr	5,2*-7,2	19-27	0,6-0,8	0,7-1,0	0,2	-
Mean Mn concen- tration, in %	0,103	0,07	0,43	0,4	0,8	20
Total Mn con- tent, million t/yr	19,1*-26,5	11,8-16,5	7,3-10,0	6,5-9,2	0,8	0,01**
Total-Mn deposi- tion rate, mg/sq cm/1000 yr	5,3*-7,4	13,4-18,8	2,7-3,7	2,9-4,1	1,6	0,02**
Total Fe-Mn concre- tion production, million t/yr	-	-	-	-	-	0,05**

*Minimum calculated river suspendate flux.

**250 billion tons of concretions formed in ocean floor ore zones under these conditions. Time range of uninterrupted concretion development: 5 million yr.

No documentation is offered to support this claim [25]. The authors' own data show that only 60% of the Al settles in the river—sea mixing zone. Al is the best proxy element to characterize lithogenic sediment behavior in general [26, p. 47]. The authors [25] could hardly claim that the geochemical mobility of Al exceeds Mn mobility in any lithogenic stage.

Gordeev's calculation [12] of 38% Mn loss from streamflow at the estuarine barrier is closest to actual conditions. It conforms to other calculations (Table 3) on Mn precipitation in the near-continental depositional area (62-64%). The estuarine barrier is the first zone of avalanche (slump-turbidite) sedimentation. The second zone of avalanche sedimentation, not present everywhere on the shelf beyond the river—sea water mixing zone, may be located at the toe of the continental slope. These sediments are absent from the slope itself.

Because solid sediment flux from streams to the ocean represents the dominant portion of the sediment load and approximately three-quarters of the Mn content (Table 1) that accumulates in the pelagic zone, it can not be determined alone by the Mn volume, deposited in the near-continental zone (Table 3). Yearly Mn deposition is also measured in the pelagic where sedimentary Mn settles from river suspendates. Stream suspendates of high Mn content, above the clarke level are the main source of Mn-enrichment in pelagic sediments in the sedimentary process. These high-Mn suspendates represent huge volumes that settle in the pelagic zone along with minor amounts of other sedimentary matter. Manganese forms high concentrations (0.44-0.55%; Table 3) in this zone. The Mn content is 6-8-times greater than in near-continental deposits and continental sedimentary rocks.

TABLE 6. Mn Distribution on Ocean Floor. 10 million tons/yr Hydrothermal Mn Flux Supplements Sedimentary-Mn Flux

Parameters	Total (mean)	Mn sedimentation areas and burial types				
		near- continen- tal (un- consoli- dated sedi- ments)	pelagic zone			
			total (sedi- ments and Fe-Mn con- cretions)	periphery (unconsol- idate) sedi- ments)	ore zones	
					unconsoli- dated sedi- ments)	
Area, million sq, km	360,2	87,6	272,6	222,6	50,0	-
Total sediments, billion t/yr	20,5*-27,8	14,6-21,3	5,9-6,5	-	-	-
Amount of non- biogenic sedi- ments	18,6*-25,9	13,9-20,6	4,6-5,3	4,45-5,1	0,2	-
Mean rate of nonbiogenic sedimentation, g/sq cm/1000 yr	5,2*-7,2	17-23	1,5-1,9	1,8-2,3	0,4	-
Mean Mn concen- tration, in %:	0,14-0,16	0,07	0,42	0,40	0,80	20
Total Mn content, million t/yr	29,1*-36,5	9,7-14,5	19,4-22,0	17,8-20,4	1,60	0,01*
Total-Mn deposi- tion rate, mg/sq cm/1000 yr	8,1-10,1	11,1-16,5	7,1-8,1	8,0-9,2	3,2	0,02*
Total Fe-Mn con- cretion production, million t/vr	-	-	-	-	-	0,05**

Notes: *Minimum calculated river suspendate flux.

**250 billion tons of concretions formed in ocean floor ore zones under these conditions. Time range of uninterrupted concretion development: 5 million yr.

DISTRIBUTION OF SEDIMENTARY Mn IN PELAGIC OCEAN AREAS

In addition to the 7.7-9.6 million tons of sedimentary Mn, 1.73 billion tons of nonbiogenic matter is deposited in the pelagic sedimentation zone (Table 3). It follows that the mean Mn content in pelagic clays may vary between 0.44-0.55%. Data on total Mn content, deposited here (8.35 million tons/yr) indicates a 0.49% mean Mn concentration in pelagic sediments. Our mean total Mn values are very similar to those, calculated independently by Lisytsin. Lisytsin's figures relate only to unconsolidated ocean deposits, not to yearly Mn accumulation in concretions and crusts.

The pelagic ocean area (272.6 million km²) is huge. Its deposits represent various lithofacies. They include pelagic deep-water red clays, miopelagic clays, transitional deep water clays; also hemipelagic sediments, outlined by the periphery of the pelagic region. Biogenic sediments also occur in the pelagic. They include carbonates and silica (radiolarians), with nonbiogenic terrigenous components. In addition, hydrothermal-sedimentary deposits occur practically throughout the entire pelagic. Massive sulfides, authigenic silicates and so-called metal-bearing sediments that contain hydrothermal Fe-hydroxides occur. Metal-bearing deposits are most widespread in a 10 million km² area [5] of the SE Pacific. Fe-Mn concretions occur in this pelagic ore belt, representing contemporary Fe-Mn ores with maximum Mn content.

Mn concentrations range widely in the pelagic sediment types. A generalized Mn-distribution chart, based on nonbiogenic components [22, 25] indicates that a minimal (<0.1%) Mn-content is typical of hemipelagic deposits that

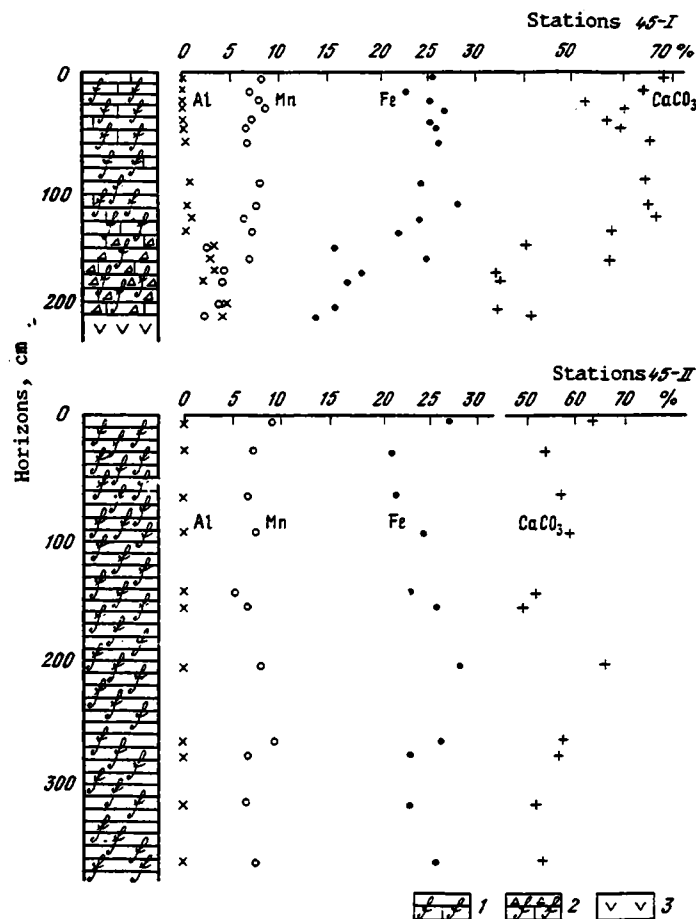


Fig. 4. Distribution of Al, Mn, Fe, and CaCO_3 in logs of metal-bearing deposits, axial zone of East Pacific Rise (17°S) [18]: 1) ore-bearing sediments; 2) metal-bearing sediments with basaltic edaphic matter admixture; 3) basalt.

rim the pelagic region (Fig. 2). Maximum (9%) values occur in metal-bearing sediments of the axial zone of the East Pacific Rise [17, 18] near springs of hydrothermal solutions. Mn concentrations in bottom sediments may reach 0.6%, locally even higher values outside hydrothermally enriched Mn-Fe metal-bearing sediment areas and within ore zones with Fe-Mn-concretions.

General distribution patterns indicate that the greatest Mn concentrations, beyond the areas of evident hydrothermal effects occur in deep basin centers, characterized by the lowest sediment accumulation rates and by Fe-Mn concretion growth. All Mn-distribution maps and cross sections indicate the same pattern in the pelagic: gradual Mn increase, at different rates, of sediments from marginal toward central areas.

Values vary in the deep basin centers that generally display high Mn concentrations. Skornyakova's Pacific Ocean data [29] are useful in establishing the Mn-content in pelagic margin deposits. So are data from the Pacific transoceanic geochemical profile [27] and other cross sections across ocean deposits between shelf and pelagic areas. The data produced a c. 0.4% Mn mean for hemipelagic deposits and miopelagic clays. This approximately equals Mn concentrations in pelagic seafloor margins. Apparently, it is close to Indian Ocean values and slightly higher than Atlantic Ocean figures.

Baturin's data [3] indicate that the mean Mn-content, recalculated for nonbiogenic matter in deep water red clays of the Pacific Ocean, equals 0.78%, in the Atlantic, 0.71%, in the eastern Indian Ocean, 1.28%, and in pelitic carbonate muds of the Pacific, 0.52%. This produced a mean Mn value of 0.75% for unconsolidated ocean sediments. A 0.8% figure is used in the following calculations.

Our data help solving the problem of Mn distribution in the pelagic ocean zone between the ocean rim zone and ore fields. In addition to the total sedimentary Mn volume that annually reaches the pelagic area (Table 3), we also require the mean Mn figure from the pelagic zone margin (0.4%) and from the ore zone (0.8%), the total yearly supply of

nonbiogenic matter to the pelagic area (1730 million tons); finally the amount of sediments in oceanic ore zones. Based on ore zone areas [3], this figure was estimated so million km². A mean absolute sedimentation rate figure of 0.2 g/cm²/1 ka was used; the yearly sediment supply to the ore zone area calculated as 100 million tons. Using this premise, the total annual Mn volume, accumulating in unconsolidated pelagic sediments is the following:

$$(1730 - 100) \cdot 0.004 + 100 \cdot 0.008 = 6.5 + 0.8 = 7.3 \text{ million tons.}$$

This value equals the amount of Mn required for the observed Mn distribution values in unconsolidated pelagic ocean sediments. This approach disregards the Fe–Mn concretion formation process. The amount of ore zone sediments, 100 million tons, represents c. 6% of the 1730 million tons total sediment weight in the pelagic. The total Mn accumulation figure may be changed if the ore zone sediment volume is doubled or halved. This manipulation produces the following annual Mn accumulation values in areas of unconsolidated pelagic sediments:

$$(1730 - 50) \cdot 0.004 + 50 \cdot 0.008 = 7.1 \text{ million tons,}$$

$$(1739 - 200) \cdot 0.004 + 200 \cdot 0.008 = 7.7 \text{ million tons.}$$

The difference between the upper and lower range limits of the Mn range (0.6 million ton) is 10%. Our calculated maximum Mn content in pelagic sediments (7.7 million tons) may be somewhat exaggerated. Unless actual field conditions are altered, the ore zone area, the Mn concentration in unconsolidated sediments of the ore zone, or the absolute sedimentation rate in this area can not double. On the other hand, in calculating the minimum value (7.1 million tons), we assumed that the mean deposition rate is 0.1 g/cm²/1000 years in the ore area. This is in agreement with available data [3, 21].

Consequently, sediments annually introduce 7-7.5 million tons of Mn to the pelagic deposition area. This conclusion ignores the process of present-day Fe–Mn ore mineralization. Comparison with data from Table 3 indicates that even minimal amounts of sedimentary Mn (7.7 million tons), introduced to the pelagic ocean with minimal influx of fluvial solid sediment discharge and pyroclastic matter, would account for the present Mn distribution pattern in ocean sediments. Calculations indicate that the figure exceeds the required Mn content slightly. If the dispersed Mn volumes, introduced into pelagic ocean deposits have exceeded 7.3 million tons/yr, the above-cited Mn volumes must have participated in Fe–Mn concretion development in sediments of oceanic ore zones.

In reviewing the distribution of sedimentary Mn in all depositional zones, slightly greater volumes of Mn were assumed buried in unconsolidated sediments following these calculations: (1) the mean Mn content (0.06%) in near-continental sediments was taken as 0.07%; (2) a somewhat higher mean Mn-content in marginal sediments of the Atlantic pelagic area (0.4%); (3) a Mn volume of 0.75 million tons/yr was used as the figure for optimal Mn influx to unconsolidated deposits of pelagic ore zones. This calculation provides a somewhat higher annual value of buried Mn.

The calculations led to the conclusion that sedimentary Mn influx into the ocean is compatible with the amount of the buried Mn that was transported to unconsolidated oceanic deposits, and also with the amount used up in ore formation.

Finally, the distribution of sedimentary Mn in bottom deposits conforms with oceanic geomorphic units, sediment volumes and with mean deposition rates (Table 4).

Before interpreting calculation results, one is reminded that a calculation error range applies to the Mn concentration intervals in the entire pelagic area, to interval values of total volumes and to Mn accumulation rates. The calculation problem relates to the uncertainty regarding the annual volume of nonbiogenic sediments that enter the ocean. Minimum values refer to minimum estimated nonbiogenic sediment volumes; maximum values, to maximum selected sediment figures. Either intermediate value of nonbiogenic sediments that annually enter the ocean, indicates mean Mn concentration, total mass figures, and accumulation rates, as calculated by the present system. The figures do apply to the entire pelagic zone, to ore zones system, as well as to areas of Fe–Mn concretion formation.

Table 4 illustrates two main points. First, the main difference that exists in the dynamics of total sediment deposition and in Mn accumulation rate changes during transition from near-continental areas toward the oceanic ore fields in open pelagic areas. When the sedimentation rate decreases by 100-150 times, the Mn accumulation rate is reduced only by 3-6 times. This type of pelagic trend is typical of the oceanic geochemistry of Mn and Mn-group elements [27, 34]. In contrast with sediments of continent margin areas, this change leads to a tenfold or even greater enrichment of oceanic pelagic deposits in Mn group elements.

Second, values of total Mn volume and accumulation rate are of prime importance in the ore zone. Mn figures are comparable with those of Fe–Mn concretions (half of the concretion Mn content) and significantly (three times) higher

than Mn in unconsolidated sediments. Pelagic ore zones experience intensive Fe—Mn concretion growth. 5-25% of the total Mn volume that enters the pelagic zone is used up in these regions.

If one accepts our minimum Mn figure (0.4 million tons) as required annually in Fe—Mn concretion and ore crust formation and assuming a 20% Mn content in ore zones, two million tons ore matter forms annually. This corresponds to a rate of 200 billion tons/100,000 yrs. The highest value cited for maximum Mn concentration in Fe—Mn concretion growth (2.3 million tons/yr), would correspond to a mean ore formation value of 115 billion tons during the Holocene Epoch.

Alternate Model for Sedimentary Mn Distribution in Pelagic Ocean Areas. Fe—Mn ore mineralization was intensive in the pelagic ore belt. High rates and young age (10-1000 ka) characterize concretion growth. Such a conclusion contradicts many growth rate calculations, based on radiometric dating. These suggest low Mn accumulation rates in the Fe—Mg concretions and concretion ages if measured in millions of years. If the old ages are correct, the yearly Mn accumulation in oceanic concretions would require consumption of only a few tens of thousands tons Mn. In this case, accumulation rates could not be calculated by the earlier method. With a required precision of 0.1 million tons/yr, the difference between maximum and minimum oceanic Mn influx values, based on previous calculations, would be 6.3 million tons/yr (Tables 1 and 3). However, the minimal flux of sediment matter to the ocean and an associated minimal accumulation of sedimentary Mn in the pelagic bottom area would result in intensive Fe—Mn concretion formation (Table 4).

Radiometric means of Fe—Mn concretion growth rate measurements in pelagic deposits are excluded from the present discussion. There are contradictions between various results. If the isotopic dates are false, then the source data on which our present Mn-supply and ocean floor distribution model is based, at least in part, are incorrect.

An ancient age of Fe—Mn concretions would require reduction in the estimated annual Mn flux to sediments of the pelagic ore zone. In adopting the suggested model of Mn distribution in sediments, there are two ways by which the Mn volume may be reduced in the pelagic zone.

The first, is reduction in the annual Mn supply to the ocean by lessened solid sediment supply by stream suspension. our minimum value of annual river suspendate flux (12.7 billion tons) provides for a 7.7 million tons/yr Mn accumulation in the pelagic ocean. Unconsolidated deposits may contain only 7.3 million tons. Using our calculation, it is apparent that 7.3 million tons/yr Mn input to the pelagic zone would only require unconsolidated pelagic sediments. Fe—Mn-concretions would not form on a large scale. With 11.8 billion tons/yr river suspendate entering the ocean, the entire Mn requirement (19.1 million tons/yr) is easily satisfied. This value is 1.1 million tons less than the previously indicated minimum Mn figure (Table 1).

The fundamental indicators of the balance of sediment matter and Mn in the ocean are the following:

Total amount of solid river sediment flux	13.0 billion tons/yr
Same, for nonbiogenic matter	18.6 billion tons/yr
Amount of sediments in pelagic zone	1.73 billion tons/yr
Total sedimentary Mn	19.1 billion tons/yr
Amount of Mn in sediments of all pelagic regions	7.3 billion tons/yr
Same, in ore zone sediments	0.8 billion tons/yr

Intensive development of Fe—Mn concretions does not take place in sediments of the entire pelagic and ore zone under these conditions during times of geochemical stability. Ore formation then would be of local, sporadic, and discontinuous quality. In preserving the developing Fe—Mn concretions on the seafloor by the hypothetical means of concretion-"floating" [15], concretion development would extract minor amounts of Mn from unconsolidated sediments in oceanic ore zones.

If ore zones of the global ocean pelagic contain a Fe—Mn concretion volume of 250 billion tons Fe—Mn concretions* and their mean age is 5 Ma, then the developing Fe—Mn concretions would require 10,000 tons/yr Mn. Provided

*Calculation of seafloor concretions (250 billion tons) was arbitrary, in adopting them for this model. The values corresponds to the mean Fe—Mn concretion productivity in the ore zone area, 5 kg/m². The mean age of the concretions is similarly arbitrary. Doubling or halving these values would not substantially alter our conclusions. Estimates on total surface concretions range between 90-1600 billion tons [4, 28, 30].

the ore zone sediments accumulate 0.8 million tons/yr Mn, only 1% of this amount, c. 0.1% of the total Mn in the pelagic deposition area enters Mn–Fe concretions during their formation. Slow concretion growth and the volume of Mn, annually extracted from unconsolidated sediments even in ore regions, result in the geochemical stability of these sediments.

However, Strakhov's suspendate sediment flux estimate, based on G. V. Lopatin (12.7 billion tons/yr), is a minimum. All others provided higher solid river sediment values [12; Table 3].

The second method, better suited to reducing Mn flux to pelagic ore zones, involves increased sediment volumes in the entire pelagic depositional area. With minor increase in the amount of Mn in the near-continental sediment accumulation area and its increase in all pelagic areas; with the stability of the sediment volumes in the ore zone, the Mn volume would be reduced in the pelagic ore zones. Changes in total Mn volume in the pelagic zone, an increase in the nonbiogenic sediment component in the pelagic are shown in Fig. 3. Increased annual nonbiogenic sediment volumes to the pelagic are marked on the abscissa on left, while the ordinate shows Mn volume changes in sediments and in Fe–Mn concretions of ore zones (Lines 3–6). on the right, changes are marked in total Mn volumes for the entire pelagic area (1) and in marginal pelagic zone sediments (2). A dashed line that parallels the abscissa (7) indicates total Mn in unconsolidated sediments of ore zones (0.8 million tons/yr, with a sediment volume of 100 million tons/yr and a 0.8% Mn concentration). The dashed line that parallels the ordinate (8) corresponds to the mass of introduced nonbiogenic sediments in the pelagic zone (1.73 billion tons/yr, based on Lisitsyn). Lines 3, 4, 5 and 6 indicate a reduction in the total Mn volume in oceanic ore zones and in the Mn incorporated annually in Fe–Mn concretions with increase in the amounts of nonbiogenic sediments in the pelagic region. Maximum and minimum sediment and Mn supply values to the pelagic zone were marked (Table 1). The intersection of Lines 4 and 5 by the abscissa, and Lines 3 and 5, by Line 7, indicate the total volumes of sediments in the pelagic zone. Unconsolidated sediments in the pelagic region preserved their geochemical characteristics in terms of Mn content (0.8% Mn). Practically no Fe–Mn concretions formed. Further increase in sediment volumes in the pelagic ocean eliminated preconditions that were employed in the geochemical model. Unconsolidated sediments received less than 0.8 million Mn/yr. Figure 3 displays the basic conclusion from these calculations. The sediment mass can not be arbitrarily increased in the pelagic depositional area without changing and, in the final analysis, destroying established geochemical principles of Mn distribution.

Data in Fig. 3 indicate that the maximum possible sediment volume in the pelagic area depends on the total volume of sediment matter that enters the ocean. It also depends on the total amount of sedimentary Mn. Based on a calculated total possible minimum river suspendate flux (11.8 billion tons/yr) and the minimum sediment matter that may enter the ocean (18.6 billion tons/yr), the pelagic sediment volume generally can not exceed 1.73 billion tons/yr. With minimum sedimentary flux to the ocean (Tables 1 and 4 19.6 billion tons nonbiogenic sediments and 20.2 million tons/yr Mn), an increase in the sediment volume only to 1.85 billion tons/yr (according to A. P. Lisitsyn, 1.73 billion tons/yr) is feasible in the pelagic deposition area. The increase is less than 10%. This sediment figure coincides with an annual 0.8 million tons Mn accumulation rate in the ore zones. However, no intensive concretion development occurred. Even if the sediment volume is increased to 1.9 billion tons/yr, the Mn flux in ore zone sediments is reduced to 0.6%, as opposed to values in western areas (0.8%).

Maximum possible volume of sediments, introduced to the ocean pelagic zone (2.4 billion tons/yr; Fig. 3) is limited by the maximum nonbiogenic sediment supply to the ocean (25.9 billion tons/yr, representing 26.5 million tons/yr Mn). The limiting figure, accordingly, is 1.4-times greater than our own figures that are based on A. P. Lisitsyn.

Data (Fig. 3) indicate that in discussing distribution of terrigenous sediment matter in near-continental and pelagic ocean areas, Strakhov [33] was mistaken. He thought that the sediment volume is nearly evenly divided between continent margin and pelagic areas. Figures by Lisitsyn, relating to the amount of sediments that annually enter the pelagic area (1.73 billion tons), probably require improvement. However, they reflect oceanic depositional conditions quite accurately. As shown, Mn distribution calculations in oceanic sediments clearly indicate that with preservation of basic geochemical characteristics of Mn, pelagic sediment volumes can not achieve extremely volumes. If sediments are evenly distributed between the nearshore and pelagic ocean areas [33] it is easy to see that, independently of the total sediment volume, the present Mn distribution pattern with its contrasting pelagic and nearshore deposits was not reflected in the calculation results. Values of mean calculated Mn content in pelagic ocean sediments ranged only between 0.14–15%.

Table 5 shows calculation results on Mn distribution in oceanic bottom sediments in absence of intensive Fe–Mn concretion development. This absence resulted from reduced solid river sediment flux, in conjunction with data on Table

1, or was due to increased pelagic sediment volumes (Table 3). Such theoretical conditions of Mn distribution pattern in pelagic deposits differ significantly from conditions under which Fe–Mn-concretion development is intensive.

In comparison with the absolute rates of sediment and Mn accumulation in pelagic zones, the pelagic effect of Mn accumulation in pelagic ore zone sediments is clear. However, other quantitative ratios (comparison with the near-continental area, with c. 100, and c. 10 values) indicated that these values represent are at least half of the values, provided by Table 4. The portion of Mn that enters Fe–Mn concretions during their formation is c. 1% of the total Mn amount, while the proportion that enters unconsolidated sediments, represents only c. 0.1% of the total amount of Mn on the pelagic ocean floor.

In a variant of these calculations (Table 5), increased pelagic sediment content was not postulated in sediments of ocean floor ore belts. The very pelagic nature of ore areas on the ocean floor could have led to such assumptions. Generally, these assumptions were confirmed by the very minor fluctuations in terrigenous sediment supply. Increased volumes of pelagic sediments, as shown by our research, are also associated with possible increases of ore zone sediment volumes. They change the general sedimentary Mn distribution pattern little. A 1.5-times increase in ore zone sediments, and in general in pelagic sediments would require transfer of an additional 0.2 million tons Mn from continental rim areas. This represents 1-2% of the total Mn volume that accumulates there. The total Mn in the pelagic zone increases only by 2-3%; this minor amount does not change the general pattern (Table 5).

ROLE OF HYDROTHERMAL SOURCES IN FORMING PELAGIC Fe–Mn CONCRETIONS

Table 2 provides calculations of the yearly hydrothermal Mn flux into the ocean. The Mn range is great (0.5-10 million tons/yr). Practically all hydrothermal solutions enter ocean in the pelagic sediment zone at depths greater than 2500 m. Mixed with deep ocean waters, they are dispersed along with them in pelagic water bodies. Due to mixing with oxygenated, low-alkalinity deep waters, in entering the hydrothermal flux Mn changes from bivalent, to a four-valent form and becomes hydrolyzed. The hydrated Mn-dioxide that forms is repeatedly fixed in fine suspendates as "jets" of suspended matter. This occurs near the Galapagos spreading center and the axial zone of the Mid Atlantic Ridge [13, 35].

Metal-bearing sediments of the SW Pacific represent the best known hydrothermal-sedimentary deposits with documented Mn and Fe components and of hydrothermal origin. They cover c. ten million km² off both sides of the East Pacific Rise. The hydrothermal fraction of the total Mn content was estimated c. 85%. Approximately 0.175 million tons Mn/yr is buried in the deposits [5]. No comparable volumes of metal-bearing deposits occur in the Indian and Atlantic Oceans. The total flux of hydrothermal Mn into unconsolidated sediments in the World Ocean does not exceed 0.5 million tons/yr.

Hydrothermal Mn in ore matter occurs as hydrothermal crusts, encrustations, and in Fe–Mn concretions in the axial belt of spreading ocean ridges and their flank facies. Fe–Mn concretions are not common and do not develop in large quantities in areas with sediments of lower metal content. The western Peru Basin and certain parts of the Guatemala Basin are exception to this. In contrast with hydrothermal Fe, with its oxide ores, marked by lanthanide elements (details forthcoming in my following article), Mn is not yet associated with any dependable diagnostic-geochemical components. Discussions on the role of hydrothermal sources during formation of pelagic Fe–Mn concretions may be only very general. The question of Mn volume in Fe–Mn concretion development is unresolved. one may estimate the proportion of hydrothermal Mn that accumulated in pelagic sediments and during ore formation in general, only by assuming that hydrothermal Mn may have been transported great distances, well beyond the distribution area of metal-bearing sediments. It was mixed with terrigenous Mn throughout all pelagic ocean areas. Mn then participated in the formation both of unconsolidated pelagic sediments and Fe–Mn concretions.

Mn Distribution Model in Oceanic Deposits; Significant Impact by Hydrothermal Flux. The model presented deals with the distribution of sedimentary Mn in pelagic ocean areas. The present paper, including Table 5, shows that in the absence of intensive Mn ore mineralization, at slow concretion- and crust growth rates the distribution pattern of only of the sedimentary Mn requires an increase in the amount of nonbiogenic sediments in pelagic oceanic areas. This is an increase from 1.73 to 2.4 billion tons/yr. Any significant hydrothermal Mn flux requires transport of sedimentary matter from near-continental to pelagic depositional areas.

Calculated parameters of ocean floor sediment accumulation and Mn redistribution (Table 6) show the potential effects of an additional 10 million tons of Mn flux from hydrothermal sources on the pelagic ocean area. Data of the Table

shows that in case of such an added Mn influx to the pelagic zone, this would basically change many existing assumptions on the mechanism of oceanic deposition and the character of Mn distribution on the ocean floor:

(1) The volume of nonbiogenic pelagic sediments (5.9-6.5 billion tons/yr) would increase by 3.5-times. In contrast with earlier calculations (1.73 billion tons/yr), the sediments represent not 7-9%, but 20-25% of the total sediment volume.

(2) Current estimates indicate that the biogenic sediment volume in the pelagic zone is comparable with the terrigenous volume (1.3 vs. 1.7 billion tons/yr, respectively). Table 6 shows that the biogenic matter represents only c. 20% of the total pelagic volume.

(3) The total Mn volume in the pelagic zone (19.4-22.0 million tons) is 2.5-times greater than Lisitsyn's figure of 8.35 million tons, obtained by chart-based calculations of Mn distribution on the seafloor.

(4) Total Mn accumulation rates (in mg/cm²/1000 yrs) in the pelagic zone correlate with such rates in near-continental areas. The value is only one-fifth of this figure if the hydrothermal impact is not calculated.

Finally, even if all present assumptions on the oceanic sedimentation mechanism, yet insufficiently known, are drastically revised, the hydrothermal Mn sources (10 million tons/yr) do represent c. 30% Mn of the oceanic total, the pelagic zone 45-52%. These figures are comparable with terrigenous values, without suggesting dominance by either category.

Impact of Hydrothermal Mn with Assumed Old Concretion Ages. The assumed role of hydrotherms in Fe-Mn ore formation can not be discussed without assigning a provisional age to the Fe-Mn concretions on the pelagic ocean floor. Calculations of the role of hydrothermal Mn thus follow two opposing scenarios: (1) slow growth of Fe-Mn concretions and their old age, and (2) intensive ore formation, quick growth, and 10-100 ka concretion age ranges.

In investigating the question, we follow Fig. 5. In the absence of an intensive Fe-Mn concretion formation process, based on sedimentary (dominantly terrigenous) Mn, in preserving the geochemical stability of pelagic deposits the volume of nonbiogenic pelagic sediments (by 1.4 times) and mean sedimentation rate should increase. ore formation is driven by very small amounts of Mn that would consume only 0.01 million tons Mn/yr. 7.3-10.0 million tons/yr of Mn is buried in the pelagic area, thus insuring geochemical stability of the sediments. Additional, hydrothermal Mn accumulation in the pelagic zone may occur only through Fe-Mn concretion formation. The dispersed Mn in sediments is not necessarily only of sedimentary origin. Hydrothermal Mn is fixed in the concretions. Mixing of sedimentary with Mn with added hydrothermal Mn destroys the geochemical stability. Due to the massive presence of the element, a continuous Fe-Mn concretion development trend, not limited in space and time, takes place. Table 5 shows that on theoretical ground, significant amounts of hydrothermal Mn may not be introduced. A flux of even only 0.1 million tons/yr hydrothermal Mn to the pelagic zone under these conditions would result in the formation of 2500 billion tons Fe-Mn concretion in 5 million years. This figure is in excess of all calculations; it is simply unrealistic. It would correspond to a concretion concentration of 50 mg/m² in all oceanic ore areas.

An even greater annual Mn supply to the pelagic zone by hydrotherms would inevitably result in intensive ore development and fast Fe-Mn concretion growth. Thus, a one million tons/yr rate of hydrothermal Mn flux to the ore zones would result in 5 billion tons concretions/ka; 500 billion tons in 100 ka. Only 50 ka would be required for the formation of the previously calculated 250 billion tons concretions in ocean floor ore zones (Table 5). Hydrothermal Mn supply to the ocean, while constant, fluctuates in terms of time and volume; probably also in concentration. This is indicated by a profile, based on cores drilled along axial zones of the East Pacific Rise. Cores 45-1 and 45-2 indicated (Fig. 4) that Mn and Fe, and importantly, CaCO₃ concentrations remained relatively constant. This proves the absence of interruptions in the hydrothermal element supply during the past 1-2 million years.

Continuous supply of Mn from hydrothermal sources at rates of 1 million tons/yr and higher, and associated with the geochemical stability of the sediments, indicate continuity in Fe-Mn concretion formation process during a well-documented time interval. This would indicate that concretions in the top meter of pelagic sediments formed continuously. However, this was not the case. Individual buried concretions and even sediment horizons with concretion layers do occur occasionally in ore zone sediment cores. Nevertheless, they are vertically separated by sediment layers of different thickness.

Thus principles that govern concretion depositions indicated the absence of significant Mn deposition from supplementary hydrothermal sources. As has been pointed out [8, 11], the question, whether the intensity of periodic ore formation had fluctuated in the past, is justified.

It follows from our data (Table 5) and discussions that, assuming old concretion ages and slow Fe-Mn concretion growth, the role of hydrothermal Mn and Fe-Mn ore formation poses the question on the volume of hydrothermal Mn. It

was transmitted to the pelagic sedimentation zone and occurs mainly dispersed in unconsolidated metal-bearing deposits. As indicated, hydrothermal Mn flux to the ocean in that case would not exceed 0.5 million tons/yr.

If hydrothermal Mn, dispersed in unconsolidated metal-bearing sediments (c. 0.5 million tons/yr; as shown above), is omitted from calculations of the mean Mn concentration in sediments of the pelagic margin and in ore zones, then the role of hydrothermal Mn in pelagic ocean sediments may be evaluated. The following numbers are used in the calculation:

$$\sim 7\% \frac{(0.5 \cdot 100)}{7.3 + 0.5} \quad \text{and} \quad \sim 5\% \frac{(0.5 \cdot 100)}{10.0 + 0.5}.$$

The hydrothermal Mn ratio in oceans, including near-continental areas is calculated as 1.8-2.6%.

Possible Role of Hydrothermal Source Matter in Fast Growth of Fe-Mn Concretions in Pelagic Ocean Regions. Calculation of ore matter sources in young seafloor concretions in oceanic ore zones, inferring fast growth rates, must start from the assumption that favorable growth conditions for fast growth do periodically recur. Marked pulses of ore matter that reach the seafloor in ore zones are required.

As earlier, calculations must be based on the premise of 250 billion tons Fe-Mn concretion deposits in ocean floor ore zones. With a 20% Mn content in the Fe-Mn concretions and their assumed age of 100 ka, 0.5 million tons/yr Mn participates in the ore-forming process. Five million tons Mn accumulated during the Holocene, in the last 10 ka. The amount of hydrothermal Mn in unconsolidated pelagic sediments must be taken into account while calculating the total hydrothermal contribution to pelagic sediments and ores. Earlier estimated, this rate is 0.5 million tons/yr.

If available calculation of the total amount of sedimentary matter and associated Mn are utilized, the maximum total sediment amount (27.8 billion tons/yr; 25.9 billion tons/yr nonbiogenic) on the ocean floor receive an annual addition of 26.5 million tons Mn. 2.3 million of this is consumed by the developing Fe-Mn concretions (Table 4). only 24 ka is needed in the formation of 250 billion tons Fe-Mn concretions. Consequently, hydrothermal Mn supply is not required in pelagic Fe-Mn ore formation; terrigenous sedimentary Mn volumes alone are sufficient. The role of hydrothermal sources may be discussed and evaluated if one assumes the post-Pleistocene age of the Fe-Mn concretions. In this case the contribution of hydrothermal Mn in pelagic zone is $(5.5 - 2.3) \cdot 100 / 9.6(5.5 - 2.3) = 25\%$. For the oceans, in general, contribution from hydrothermal sources was calculated as $(5.5 - 2.3) \cdot 100 / 26.5 + (5.5 - 2.3) = 11\%$. The calculations indicate that, even assuming an unrealistic very young age for the Fe-Mn concretions in ore zone surface sediments, hydrothermal Mn would represent only one-fourth of the total supply. It is of minor importance.

The author admits to the highly tenuous character of the balance calculations. Many underlying data will have to be refined. The calculated hydrothermal Mn volumes probably will change. Nevertheless, basic conclusions will be confirmed. These include the predominance of terrigenous sources over hydrothermal (volcanogenic) ones in the Mn flux to the ocean that involves Mn supply to pelagic deposition areas and a role in Mn-ore forming processes.

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GEOCHEMICAL SOIL CONDITIONS OF ASSOCIATED LANDSCAPES, CENTRAL PRECAUCASUS

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Redox and pH conditions in soils; newly formed substances and sulfur isotope composition in soils have been studied in catena landscape areas on the east slope of the Stavropol' Uplands. Newly formed gypsum and carbonates in the soils are represented by varying morphological and genetic types. Their distribution, just as the redox-pH conditions depend on the geochemical positions of soils in the landscape and reflect dynamics of the soil development conditions. A wide variation in the isotope composition of sulfate salts points to polygenetic salt sources in soils of these landscape units. The three salt generations include evaporites, secondary marine sulfate deposits, and salts in continental loess rocks and soils. Soil and loess salts predominate in salt flux. Salts of marine deposits are of lesser importance.

Study of the geochemical structure of landscapes [6] provides the necessary data for establishing a theory on the ancient and present processes of landscape evolution and landscape functions. The conceptual and methodological foundation of these studies was developed by Polynov, Strakhov, Kovda, Perel'man, and Glazovskaya, with various theoretical and practical applications. Presently, the geochemical structure of the landscape is described essentially in terms of a relatively simple chemical components. Less attention is being paid to complexes and forms of chemical elements, although their role in landscape-geochemical processes, especially in soil forming processes, is not less important.

This fact has stimulated workers to undertake a complex study of soil-geochemical conditions and of the behavior of various mineral complexes and their forms. The work was carried on by the example of associated landscapes in the steppe zone. Based on experiment results, the purpose of my work was to (1) determine formation trends of mineral matter in soils, with regard to their position in the landscape; (2) clarify large scales and forms of steppe landscape geochemical associations; (3) identify indicators of mineral substances in soils, diagnostic of specific formation processes in various geochemical conditions in landscapes.

This paper is the first in a series. Behavior of minerals in coarse clay mineral fractions will be discussed in forthcoming publications.

The study was focused on soil macrocatena on the east slope of the Stavropol' Uplands macrocatena, between Prikalauusk Heights and the Otkaznensk water divide. In conformity with the topographic slope, this macrocatena generally trends in a NW – SE direction.

The formation of the Stavropol' Uplands' associated with the rise of the Greater Caucasus. Since the Neogene it has undergone increasingly intensive uplift. A sea covered in late Miocene times and submarine plains formed. After the Sarmatian, the Uplift region was raised and dissected. As the result, the present Stavropol' Plateau is a substantially uplifted, primary marine plain and represents a basic relief level that has undergone intensive erosion in post-Pontian times.

The relief of the eastern Stavropol' Uplands slope is a system of parallel, low ridges that slope toward the SE. Rivers of low discharge, occasionally intermittent, occupy lowland positions. The distances between the ridges range from 4-5 km in the Prikalauusk Heights, to 10 km in the eastern macrocatena area where the ridges level out.

TABLE 1. Natural Condition Characteristics and Macrocatena Soils

Section number	Soil designation	Position on surface categories	Absolute elevation	Moisture index	Parent rock	Thickness of humus horizon, cm;	Organic carbon content in layer	Weighted mean of particles in section, % composition		Depth of HCl- effervescence, in cm	Ground water level (range of seasonal fluctuations), in m;
								<0,001	<0,01		
Mesocatena 1											
18	Type chernozem	Drainage divide surface	540	0,9	Eluvial clay	110	3,1	35,4	57,8	55	>10
19	Compact chernozem-prairie soil	Slope	480	0,9	Eluvial-talus clay	102	3,6	45,6	65,2	60	0,8 (0,5-1,5)
20	Alluvial prairie soil	Floodplain	420	0,9	Alluvium	88	1,9	31,7	40,7	in land surface	0,6 (0,6-1,2)
Mesocatena 2											
21	Common chernozem	Drainage divide surface	440	0,8	Eluvial-talus clay	95	2,8	37,8	49,8	Same	>10
22	Same	Slope	420	0,8	Same	96	2,2	37,1	51,3	"	>10
23	Alluvial prairie soil	Floodplain	350	0,8	Alluvium	88	4,6	26,2	47,2	"	0,7 (0,5-1,0)
Mesocatena 3											
11	Chernozem, common, deeply salt-saturated;	Drainage divide surface	320	0,5-0,7	Loess loam	104	2,0	23,6	38,7	"	>10
16	Same	Slope	280	0,7	Same	81	1,5	24,3	38,2	"	>10
15	Alluvial, peaty	High-level floodplain	240	0,7	Alluvium	104	2,2	37,1	67,7	"	5
Mesocatena 4											
32	Dark chestnut soil	Drainage divide surface	200	0,4-0,5	Loess loam	44	1,2	24,3	38,1	"	>10
31	Same	Slope	190	0,5	Same	35	1,3	22,6	44,9	"	>10
33	Floodplain-prairie soil	Floodplain	170	0,5	Alluvium	-	2,2	26,3	41,5	"	0,5

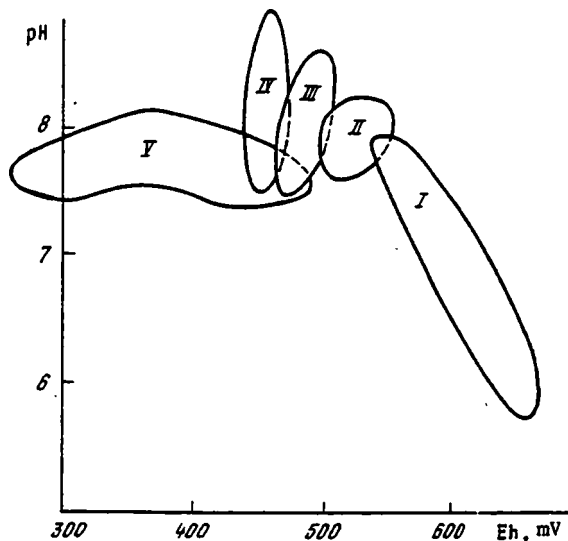


Fig. 1. Oxidizing and acidic-alkaline conditions in catena soils. I, II, III, and IV) soils of drainage divides and slopes of corresponding mesocatenas; V) soils of floodplains of all mesocatenas.

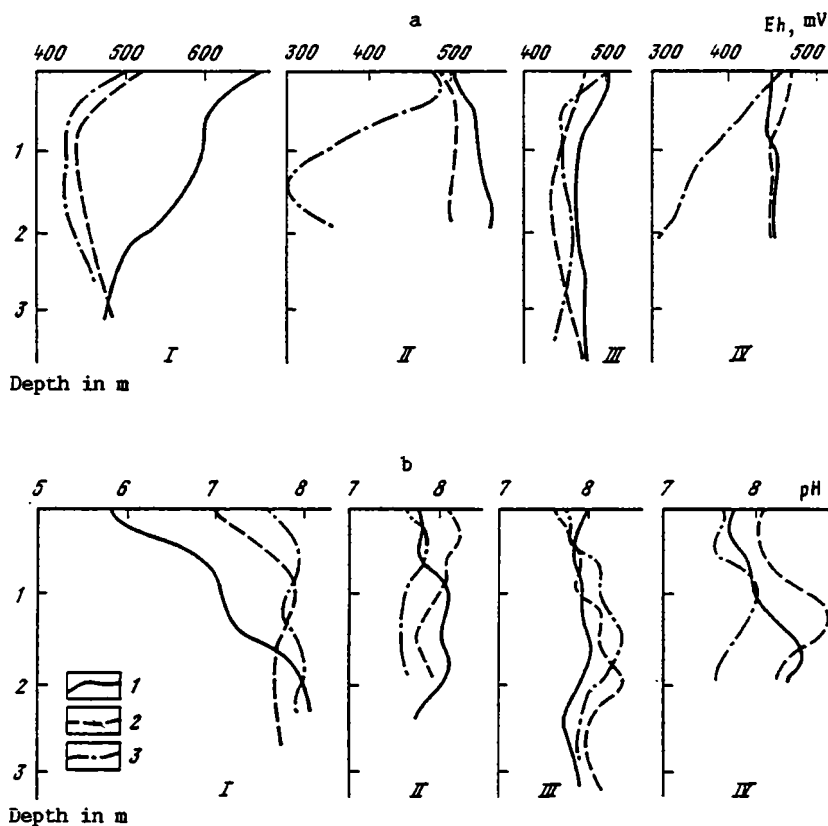


Fig. 2. Redox values (a) and pH values (b) in drainage divide soil profiles (1), slopes (2) and floodplains (3).

The study area contains two groups of soil-forming rocks. The first includes Paleogene–Neogene marine deposits, with dominant clays of the Maikop Formation. They underlie the higher, western part of the slope. The second group represents continental, loesslike sediments the underlie the lower eastern slope areas.

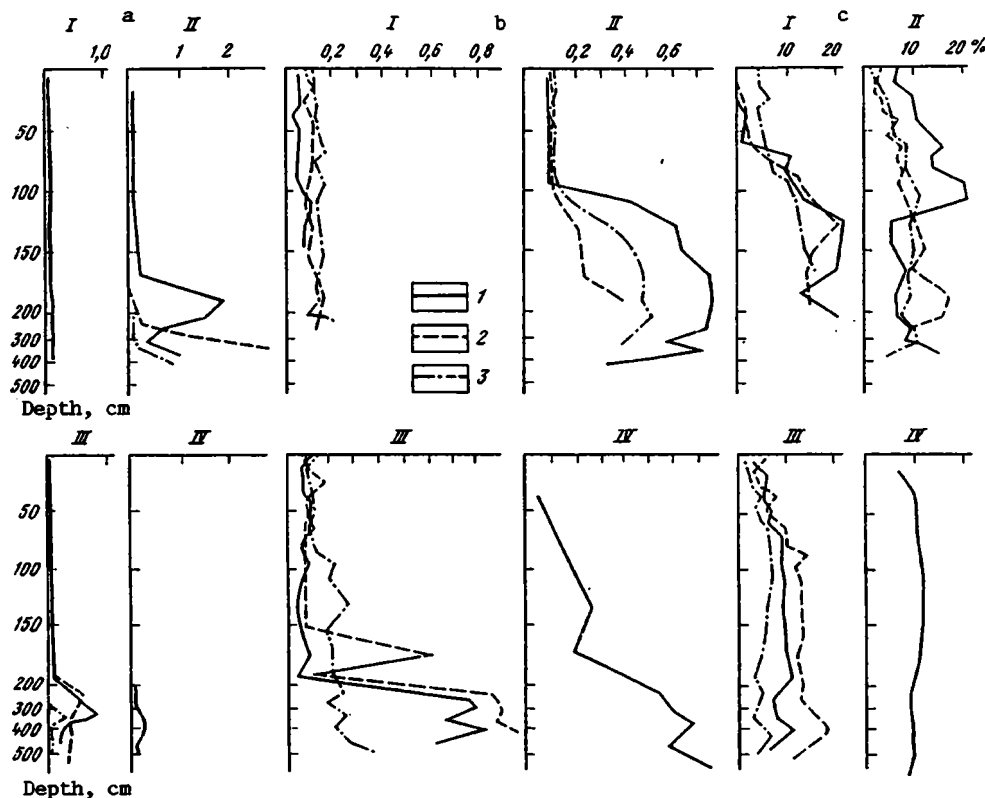


Fig. 3. Composition of gypsum (a), water-soluble soils (b); carbonates (c); in water-divide soils (1); slopes (2); and floodplains (3) of catenas, in percentages; I-IV) mesocatenas number.

In general, the macrocatena includes eluvial transeuvial and transaccumulational landscapes that formed at different levels of the macrorelief. Each landscape, in turn, represents an associated geochemical landscape; a mesocatenas complex that includes water divide, slope, and floodplain. Four mesocatenas were studied. The first occurs in an eluvial landscape on the Prikalaussk Heights, 5 km south of Kruglolesskoe village of the Aleksandrovsk region, Stavropol' District. Mesocatenas 2 in transeuvial landscape occurs 17 km from Prikalaussk Heights, km SW of Ledokhovichi Farm, Aleksandrovsk region. Mesocatenas 3 is transeuvial landscape, 39 km from Mesocatenas 1 and 4 km NE of Sablinskoe Village, Aleksandrovsk region. Mesocatenas 4 occurs in the transaccumulational landscape, 100 km from Mesocatenas 1, 13 km west of the town of Zelenokumsk, Sovetsk area. Drillholes and trench cuts in the water divide, slope, and floodplain of each mesocatenas were used to study the soils and their parent rocks.

Climatic conditions of the macrocatenas change with lower topographic positions above sea level. The highest areas have a mean annual temperature of 8.6°C, the lowest ones, -9.2°C. The cumulative value of temperatures above 10°C in the Mesocatenas 1 area was 2800-3000°C; for Mesocatenas 4, it was over 3200°C; soils of Mesocatenas 1 receive 470-480 mm annual precipitation, Mesocatenas 4, 460 mm [2]. Such climatic differences led to variable soil types and subtypes.

Soil characteristics under natural conditions of mesocatenas are shown in Table 1.

Each redox measurement in the field was triplicated. Electrodes TPL-01M and EVL-1M3 were employed. Redox and temperature measurements at natural moisture levels in the field were performed immediately after the samples were obtained. Orion Research Model 201 electrode was used in pH measurements. Right after samples were taken, pH was determined in a 1:1 water:soil paste-mix. Measurements of dynamic soil parameters (redox and pH) in the mesocatenas and composition of surface and ground waters on the Mokryi Karamyk River and its distributaries were conducted in August, 1988 in a one-week period under steady weather conditions. Ethyl alcohol replaces soil solutions [11, 16]. Salt composition in soils was determined by replicating five times each measurement. Gypsum, carbonates, and easily soluble salts in salt and water [1] were analyzed by standard methods. Sulfates and easily-soluble salts and gypsum samples for mass spectrometer analysis were taken from soil samples. They were analyzed by standard methods [1] consecutively by water and HCl-extraction. Precipitation in the form of Ba-sulfate followed. Preparations of sulfate for mass spectrometer analysis was based on [17]. Determination of the interrelationships between stable S-isotopes (SSI) was by spectrometer MI-1330. The

SSI measurements were shown as $\delta^{34}\text{S}\%$ values that characterize the relative enrichment of the sample by ^{34}S heavy isotope in relation to meteoric standard: according to this standard, $\delta^{34}\text{S}$ equals zero. Carbonate inclusions and newly formed minerals were studied by optical microscopy in the light (low density) fraction of the coarse soil fraction, separated by a sieve set of 1-0.05-mm mesh-diameter sieves. The size fraction subsequently was separated by bromoform (density – 2.9 g/cm³).

Study Results. Discussions. Redox conditions and reaction of the medium, on one hand, are the most important factors in the formation of minor substances of soils. On the other, alteration trend in soil components are the most important determinants. This is clearly shown in the geochemical landscape. From eluvial to accumulation parts of macrocatenas a clearcut trend of pH increase and redox reduction prevails. The redox value range in the soil profile narrows (Fig. 1). pH change from eluvial, toward accumulative macrocatenas is in agreement with ample data, available from geochemical landscapes in the steppe zone. Prevailing theories note reverse relationships between moisture content, biogenic character of soils and redox values: a redox increase trend would be expected from eluvial parts of the catena to accumulative ones. This is not the case. The pattern that actually exists apparently is caused by the hitherto poorly known role of atmospheric precipitation as source of oxygen in soils and a geochemical link with redox conditions.

The soil solution system $-\text{O}_2 - \text{H}^+$ is an essential regulator of the redox system in the studied automorph soils [9]. Consequently, the oxidized state of these soils is basically related to precipitation-introduced oxygen. Soils in the eluvial parts of the macrocatena receive more oxygen through atmospheric precipitation. Due to its eluvial position in the landscape, the soil unit is well drained. Water does not stagnate in the soils. This may result in anaerobic processes in subordinate-landscape soils. Under more arid conditions the soils receive less precipitation and, correspondingly, less oxygen. Moisture loss slows down and, consequently, the soil matter becomes less oxidized.

Alluvial soils occupy a special place in the pH–redox system (Fig. 1). In contrast with the automorphous soil series, a wider range of redox values and narrower pH range characterize them. The redox-regulating system of hydromorphic soils form under more complex conditions than automorph soils do. Moisture may stagnate in these soils and biochemical processes operate under unaerobic conditions. Solid and liquid matter is introduced by the flux. As in automorphous soils, a trend toward reduced redox values is also noted from the higher to the lower parts of the macrocatena to the lower. In addition to the introduction of atmospheric moisture that determines this trend in water divide soils, in alluvial soils apparently it is also associated with reduced oxygen saturation of the surface and ground waters. This fact is in proportion to water movement from eluvial and accumulative landscapes.

In establishing the general landscape patterns of pH and redox development, we must review distribution characteristics of these parameters along the soil profile as they relate to the position of soil in the geochemical system of the associated landscapes. Figure 2 shows that this distribution pattern is different in autonomous and subordinate landscapes. The largest redox and pH values occurred in eluvial landscapes in soil profiles typical of the eluvial landscape. This occurred in Mesocatena 1 in which conditions favor relatively deep saturation by atmospheric precipitates and leaching of the soil profile. This process is best expressed in the water divide surface (Section, 18 where soil have relatively high redox values) in thick beds and relatively low pH in the upper half meter. In the soil absorbing complex (SAC/PPK) the presence of hydrogen was notable. Hydrolytic acidity in soil horizon A (topsoil) was 2.7 mg equiv./100 g. Unweathered Paleogene–Neogene clays, parent beds of this soil, displayed a pH range of 7.4–8.6 [12]. Clearly, chernozem-type eluvial soil formation conditions that led to intensive changes of redox and pH conditions in soil-forming rocks. The present example is the best for eluvial conditions; unique and typical of the soil complex.

Subordinate landscape soils of the autonomous soil series did not include horizons with high redox and low pH values on water divides (Sections 21, 11, 32), slopes (Sections 22, 16, 31), and floodplains (Section 15). These values were relatively uniform along the profile. In hydromorphic soils of the slope (Section 19) and floodplain (Sections 23, 33) the pattern was entirely different and strongly depended on geochemical transport processes of the soil matter. The soil profile redox conditions became differentiated. Different soil sectors were subjected to different influences.

Oxygen, not only from the atmosphere but also from ground water flow from higher-lying regions regulated the redox system. The impact of substances that influence redox and pH conditions in ground water flow depends on flow duration and the presence of given geochemical barrier along the flow path. Mesocatena 1, where ground waters accumulated, has limited areal extent. Geochemical barriers, where the dissolved oxygen content could have been dissipated, were absent from the mesocatena area. Slope and floodplain soils had relatively high redox values even in water-saturated parts of the profile (Fig. 2a). However, a significant reduction in the soil redox values from the western divide toward the floodplain apparently indicates partial impact by oxygen that was dissolved in ground waters as waters flowed downslope

in conformity with the surface relief. Increase in the same direction in anaerobic conditions, may be an additional reason. Redox reduction is even more marked in the water-saturated parts of the floodplain, at lower elevations than Mesocatenas 2 and 4. Generally, hydromorphic soils of transitional landscapes (Mesocatenas 2 and 4) are even more reducing than floodplain soils of the eluvial part of the macrocatena (Mesocatena 1). Water flow rates are relatively high here. Initiation of ground water flow in the proximity leads to intensive oxygen saturation of the ground waters.

Redox and pH conditions thus are significant in defining soil conditions in the associated geochemical landscapes. Their impact may be superimposed on the amount of moisture content and biological activity. Alluvial landscapes thus are characterized by more intensive oxidation and, in comparison with subordinate-landscape soils, by an even higher moisture and biogenic-component content. This results from greater oxygen influx from atmospheric precipitation and the better drainage that occurs in eluvial landscapes. Soil position in the associated landscape significantly determines the redox and pH conditions in each soil profile. Consequently, mineral alteration conditions in various steppe zone landscapes vary greatly during soil formation.

In classifying geochemical conditions of soil formation in associated landscapes, the mineral components are essential. First, the geochemistry of the simplest and most mobile soil components (water-soluble salts) are reviewed from the moment of their appearance in the study area and until their introduction to soils of recent landscapes.

A high degree of salt content and active salt migration characterize landscapes in the central Precaucasus. Significant salt concentrations are widespread in pre-Quaternary deposits that form the Stavropol' Uplands. A maximum 2-3% content of easily soluble salts, sulfate-chlorite, and chlorite-sulfate, of Ca-Na composition and maximum 5-10% gypsum content occurs. High sulfate salt content was found in blanketing loesslike deposits on Uplands slopes. The mineral content in the widespread ground waters amounts to a few tenths of one gram per liter. The accumulative landscapes include self-contained salt lakes and widespread salt soils.

In the studied catena area the dissolved mineral content in ground waters ranged between 0.5-30.5 g/liter; in river waters, between 0.5-15.7 g/liter. Automorphic soils, eluvial and transaccumulative macrocatena landscapes generally are characterized by eluvial salt profiles (Fig. 3a, b). These soils at 100-350 cm depth contain minor amounts of sulfate-hydrocarbonate salt with Ca. Beneath, a salt-rich (gypsum-bearing) residual accumulative horizon occurs, with easily soluble chlorides-sulfates and sulfates, Ca-Na-salts and gypsum, with concentrations of a few percentages. Salts also occur in floodplain soils in eluvial soils, less often in accumulative soils. The chloride content increases in salts. Morphologically notable precipitation forms of easily soluble salts were absent. Gypsum-type new mineralizations of the studied salts are most varied and resulted from the dynamics of their formation regime. Two main generations of newly formed minerals develop generally: coarse-crystalline "old" forms (druses, rosettes, nests, single crystals) and "younger" ones with dispersed inclusions that developed during recrystallization of minerals (dots, veins, cutans, filaments). Indications of recrystallized gypsumlike new formations, soil profile differentiation, and a high (maximum 200 μg equiv./liter) sulfate content in soil solutions and ground waters indicate active sulfate migration in this landscape area. Various gypsum types indicate that periodic changes did take place in the soil-forming conditions. Earlier studies of sulfur isotope composition (SIC) in gypsum-type new mineralizations of various gypsum generations [15] have shown that within a single soil the various gypsum generations display identical isotope ratios. This suggests an identical isotope source and no substantial changes in geochemical conditions throughout their history. No other sulfur source has been indicated by the data available.

Study of gypsum crystals of various generations under electron microscope [15] indicated that solution processes are typical in old cryptocrystalline forms. The "young" forms occur either in active growth stage or carry traces of crystal growth and dissolution. This suggests alternating soil-forming conditions. Coarse-crystalline gypsum generations that apparently formed in a stable water regime, as the result became unstable, were converted, and through seasonal wetting-drying processes were recrystallized into more dispersed forms. Unstable conditions did not favor growth of large crystals [14]. Dispersed gypsum crystals may have formed through seasonal desiccation of soils at greater depths. Soil solutions were rapidly concentrated and small crystals precipitated. The process may have been climate-related. During the last four millennia since the Atlantic climatic optimum; it has turned drier. Various gypsum generations may correspond to different stages during this process.

Soils, soil-forming rocks and rocks that underlie the macrocatena contain large quantities of carbonates (maximum 20% CaCO_3 content). Pedogenic, newly formed mineralizations belong to various morphotypes. The most widespread are mildewlike, impregnations, powdery precipitates, mottles of different shapes and configurations, encrusted forms, efflorescences, pseudomycelia, primary veins, pastelike smears, etc. Less frequent are concretions and crust-precipitates;

loess with lime nodules, lime nodules, and crusts of detrital rock fragments. Various generations of newly formed limey matter in soils reflected varied processes and formation conditions. The presence of young pore fills and other dispersed carbonate forms indicate high concentrations of corresponding ions in soil solution and ground waters. The high organic content in soils and the differentiated state of carbonate profile (Fig. 3c) indicate active migration of carbonates in soils and macrocatena landscapes.

In addition to cited pedogenic limey concretions, in most studied soils nonsoil carbonate inclusions also occur. These are fragments of aragonitic molluscan shells, fragments of marine chemical-sedimentary and biogenic limestones, 0.05-2 cm in diameter. Lime fragments usually are strongly weathered, partly decomposed. An unconsolidated, white crust of newly formed carbonate often occurs on their lower surfaces and inside the fractures. Significant concentrations of such fragments in certain soils and indications of their degradation (weathering) in the soil profile led to the assumption that part of pedogenic carbonates there formed mostly through reworking of limestone fragment of soil-forming parent rocks. A microscopic study of the coarse fraction resulted in the same conclusion. Carbonates in the light soil fraction are represented both by dense, rounded relict limestone fragments of different dimensions and by typical pedogenic new formations (Table 2). The presence of relict All soils of the macrocatena contained relict fragments. Their concentrations vary within a wide range (0.004-14% of the soil mass). Their distribution is uneven within the soil profile, generally increasing toward and in the lower horizons. Concentration variations apparently are due to differences in the colluvial source matter and their different weathering rates in different soils and soil horizons. Thus, their lowest concentrations occur in the most leached water divide soils of Mesocatena 1, with low pH values.

Newly formed pedogenic carbonate mineralizations of the light fraction consist of white, unconsolidated, irregularly shaped aggregates, 0.1-0.25 mm in size, formed in pores and as crusts. In the discussed process reorganization of the soil involves partial decomposition of loosely aggregated inclusions and only the mechanically most stable matter enters the light fraction. These are unevenly distributed throughout the soils. In strongly leached soil profiles of Mesocatena 1 (Section 18) they are absent from the upper soil horizons. Their greatest concentrations (2.3-7.4%) occur at 140-180-cm depth. In water divide soils of Mesocatenas 2 and 3, the newly formed pedogenic matter is practically absent from the light fraction. Their concentration increases in soils of transitional-accumulational landscapes (Mesocatena 4) where the matter occurs in the top 1-m interval (0.4-3.4%).

In addition to conventional approaches, stable S-isotope geochemical methods are also required in the clarification of salt geochemistry and the history of salt behavior in soils of the associated landscapes. Sulfur is used as an indicator: it enters sulfates very commonly and is the dominant water-soluble components of steppe and dry-steep soils. This makes it representative of the entire complex of water-soluble salts and landscapes in this geochemical study.

Sulfur compounds are known to have different geochemical histories and to differ in their isotope composition. In various natural compounds, the isotope composition range essentially is 100‰ [19, 20]. The isotope range in field samples usually is 70‰ [13].

A relatively stable isotope composition and heavy sulfur isotope enrichment, when compared with atmospheric standards, is displayed by sulfates in the World ocean. The $\delta^{34}\text{S}$ range is +18.9-20.8‰ [17, 18]. In evaporites of various ages the S is also enriched in heavy isotopes with a range of $\delta^{34}\text{S} = +10$ -32‰ [8, 10, 19]. S in sedimentary rock sulfates, as a rule, is significantly enriched in light isotopes, attaining negative $\delta^{34}\text{S}$ values. A significant variation in S isotope composition (SIC) occurs in organic matter of various ages. The $\delta^{34}\text{S}$ range is -23.0 to +12.9‰ [13, 20].

The $\delta^{34}\text{S}$ -range in soils, rocks and natural waters of the macrocatena is quite broad (45‰; Table 3). SIC values identified three sulfate generations of various genetic background. The $\delta^{34}\text{S} = +24.7$ -26.0‰ values identify marine evaporites. These occur as gypsum layers and Na-sulfates, dispersed throughout the rocks. These values were obtained from Paleogene-Neogene marine deposits, unaffected by soil development. They include the upper portion of the macrocatena. The other SO_4 -generations, associated with the same marine deposits are of lighter SIC ($\delta^{34}\text{S} = -19.0$ -5.4‰). Secondary sulfates formed through oxidation of sulfide minerals of sedimentary rocks. These occur in large amount; S, dispersed in pyrites in clayey rocks, represent the dominant portion of the total S content in sediment deposits and rocks. The SIC value was 0.385‰. On the Skifsk Platform [7].

Third generation sulfates in macrocatena areas are the most widespread. Values of $\delta^{34}\text{S} = +4.9$ to +7.5‰ occur. These SIC values are typical of salt horizons in soils and the underlying loesslike deposits to a depth of 30 m. They are the basic sulfate reserves in the distribution area of loesslike rocks in the upper salt-bearing accumulation horizon of soils that formed in Cenozoic marine deposits in Mesocatenas 1 and 2. There are significant S-isotope differences between the

"soil-loess" sulfates (first salt horizon-beneath the surface) and the lower sulfate evaporite generations. These indicate absence of any genetic relationship between them (Table 3).

Sulfur isotope data thus indicate different origins for water-soluble salts on the east slope of the Stavropol' Uplands. They were in part deposited during their concentration and transformation in marine waters in bottom sediments of the paleobasins. In part, they were transported by subsequent continental processes, to be discussed at the end of the paper. Which were the processes that resulted in further migration of water-soluble salts that led to the present landscape configuration? First, a basic change occurred in the transport process of water-soluble salts. Their composition and distribution in the soil belt indicates the current predominance of salt export. The Stavropol' Uplands and their slopes in the 200-600 m elevation range above sea level represent an area of previous salt accumulation. Later, the area changed to net salt exporter and salt was lost. Presently, salt is being exported from here to adjacent areas.

The proportion of a given S generation in the salt flux from various parts of the macrocatena may be determined from comparison of S isotope values in natural waters. This represents an integrated system of the overlying salts (Table 3). In natural waters in the distribution area of marine deposits (Mesocatena 1) sulfur is enriched in light kations, corresponding to the isotope composition of secondary sulfates that form during oxidation of minerals, dispersed in clayey rocks. The geochemical aspect of the landscape was responsible for the redox conditions and dominantly eluvial processes. A well-defined oxidation zone occurred, with 500-700 mV values. The sulfate fraction, represented by relatively heavy S isotopes, did not play an important role. CIS data indicate that the total salt flux from the Stavropol' Uplands in the studied region, where minor streams enter the Kuma River (Mesocatena 4) is essentially represented by salts from loesslike sediments.

To what extent are the above-discussed leaching processes in the subject area displayed in macrocatena landscape units? We must first examine the distribution of water-soluble components in the soil profile. Figure 3b shows that water-soluble salts have been leached from the macrocatena's soil profiles. The depth and degree of leaching was determined by the position of soils in the landscape and soil-forming characteristics of rocks from which the soil formed. As expected, soil units in geochemically lower positions were less leached in the distribution areas of some of the studied rocks. The thickness of leached beds in the upper part of the macrocatena in the water divide surface of Mesocatena 1 was 3 m and salt maxima were absent. These rock units in the water divide of Mesocatena 2 were leached of salts to a depth of only 1 m. A c. 1% salt maximum occurred at c. 2-m depth. Similar trends were also found in the area of loesslike deposits (water divide of Mesocatenas 3 and 4).

Migration direction of a given indicator element is an important feature in the geochemical landscape. It is provided by the relationship between element concentration values in eluvial and supra-aqueous-landscape units. Comparison between concentrations of easily soluble salts in the salt maximum at 2-4 m depth indicate that the salt content in soil units of each mesocatena area exceeds floodplain values. Such a pattern of components between morphological units of autonomous and subordinate landscape units is the opposite of the expected. This indicates that the entire investigated geochemical landscape is represented by the macrocatena. Conditions are the same for the less mobile gypsum and calcite components (Figs. 3a, c). As noted earlier, gypsum and carbonates in soils of the macrocatena actively migrate and participate in the soil development cycle. Most often, the distribution patterns of these components in the soils is also characterized by eluvial profiles. Therefore, as in the case of easily-soluble components, in comparison with eluvial landscapes, neither in the mesocatenas, nor in the macrocatenas has significant gypsum and carbonate accumulation taken place in accumulative landscape units. The geochemical landscapes of macrocatenas, in comparison with less mobile salts (carbonates and gypsum), are thus eluvial in nature.

Our geochemical studies indicated that the sulfur isotope spectra in the sulfates form independently of the character of underlying parent rocks in all macrocatena soils that include the first salt horizon beneath the surface. They are similar in composition and display narrow composition ranges. Sulfates in these rocks displayed a S isotope composition that is identical to sulfates in loess-like rocks, to a depth of 30 m beneath the surface. This fact indicates a uniform, loesslike soil genesis of the salt, with $\delta^{34}\text{S}$ values of +4.9 to +7.7%. They formed from the same sulfur source.

The presence of sulfates of the loess-soil generation in soils that developed on Paleogene-Neogene marine deposits in the highest part of the macrocatena, indicates the general regional accumulation of these salts. The salts were introduced from the atmosphere by eolian means or as atmospheric precipitates. Introduction of salts in autonomous landscapes, outlined by deep incision, through ground water flow did not take place. Salts of Paleogene soil units were of polygenetic origins. The upper interval had atmospheric and eolian genesis; the lower developed from salts of marine evaporites and secondary sulfates (Table 3).

TABLE 2. Composition of Carbonate Inclusions in the >0.05-mm Soil Fraction, in Percentages of Soil Mass

Section number (geomorphologic position)	Depth of horizon, in cm	Limestone fragments	Pedogenic components
18 (water-divide)	A _{top} , 0-24	0,006	Absent
	A ₁ , 24-50	Absent	"
	AB, 50-135	"	0,50
	B, 140-160	0,03	7,39
	C, 160-180	Absent	2,27
20 (floodplain)	A ₁ , 0-30	1,13	Absent
21 (water-divide)	A _{top} , 0-26	1,23	0,01
	A ₁ , 26-49	6,39	Absent
	AB, 49-79	2,02	"
	B, 79-123	14,82	"
	BC, 123-140	2,24	"
	C, 140-160	7,96	"
11 (water-divide)	A _{top} , 0-20	Absent	"
	A ₁ , 20-53	0,02	"
	AB, 53-95	0,11	"
	B, 95-119	0,16	"
	B _K , 119-170	0,81	"
	C, 250-300	Absent	"
32 (water-divide)	A _{top} , 0-26	0,004	0,11
	A ₁ , 26-44	Absent	0,38
	B ₁ , 44-63	"	0,37
	B ₂ , 63-95	"	0,37
	BC, 95-123	0,60	Absent
	C, 123-150	0,27	"
33 (floodplain)	A ₁ , 0-30	0,004	0,52

TABLE 3. Sulfur Isotope Composition in Sulfates in Landscapes of the East Slope, Stavropol' Upland

Landscapes component	Sample interval, in m	Composition, in %	$\delta^{34}\text{S}$, ‰
Distribution areas of Pre-Quaternary marine, soil-forming clay rocks			
First salty soil horizons below surface, on marine clays	1,4-2,0	1,8	+4,9 + +6,7
Salts of marine clays, unaffected by soil development			
evaporite sulfates	3,0-3,5	0,35	+24,0 + +26,0
secondary sulfates	10,0-15,0	1,3	-5,4 + -19,0
Ground and surface waters;	-	0,05	-0,7 + +1,6
Distribution areas of loess-like soil-forming rocks			
Salt horizons in soils	2,0-2,5	1,1	+6,0 + +6,3
Layers of underlying loess-like rocks	6-30	0,5-2,0	+6,4 + +7,6
Ground and surface waters	-	0,25	+6,7

What was the source soil-loess generation salts? We sources in the area. The sulfate isotope composition of the most important salt concentrate must consider the sulfate isotope content in the Volga River is +5‰ [4]; for the Caspian Sea the range is +9 to +13‰, for solonchaks of the western Precaucasus, +3.0 to +15‰. SIC in the present salt flux in the Caucasus (Terek, Malka, Baksan and Ardon Rivers) display a range of +12 to +14‰; the ground and surface water flow from the area of Paleogene and Neogene clay display a range of -2 to +2‰. The isotope composition of Cenozoic marine rocks that underlie loess varies greatly even within a single section (-19 to +26‰). Despite the wide spread, it is essentially characterized by negative values that correspond to secondary sulfates.

A single salt source can not be established when comparing these data with SIC values of loess-soil generations. In contrast with earlier suggested, calculated sulfate sources, the SIC values in loess units and loesslike deposits range within a narrow interval, both in terms of depth within a given section and for loess units of various region. They do not depend on relief and source characteristics. Consequently, none of these sources account directly for formation of sulfates in loess deposits. Only indirect supply methods, applicable to loess units alone were available. Matter from various sulfur sources became homogenized and the SIC value stabilized in a loess-source reservoir.

Apparently, the primary source of the soil-loess salt generation was a reservoir that received salt flux from various sources and in which mixing has taken place. The west Precaucasus region was such a prime reservoir. Presently it occupies the position of a regional accumulator. Easterly winds carried salt to high-lying western areas. Apparently, this occurred concurrently with formation of loess deposits. Loess and salt had uniform SIC throughout this sediment unit. Earlier publications have already noted the transport of salt and silicate matter to the Precaucasus by easterly winds [3, 5].

Our research results apply only to salt components of loess, thus confirming the theory that they were derived as salt dust from the Precaspian Lowland. The source of the silicate matter in loess, possibly of different origin and introduced by different methods to the sediments, will be discussed in forthcoming papers.

Salts of atmospheric precipitates may have been among the possible sulfate sources of the soils. The mean CIS value is $+7.1\%$ [7] in sulfates in various parts of the Rostov region. Due to the nonflushing water regime of the soils, sulfates that enter soil via rain and snow may accumulate at the lower boundary of percolation. They form a salt horizon over an extended time period. However, a large portion of the sulfur in atmospheric precipitates is of terrigenous origin. Evidently, it forms from the same sources (solonchaks) as salts of eolian origin do. This indicates general origins (solonchaks) and the atmospheric transport routes of salts in soils of autonomous landscapes.

(1) Redox and pH conditions in soils are determined by soil positions in the geochemical landscape. The impact may cover the moisture content and biological activity. Very varied conditions of mineral alteration prevail during soil development in landscape units of steppe zones.

(2) Three major salt categories occur in the central Precaucasus area: (1) marine evaporite; (2) secondary sulfates formed by sulfide mineral oxidation in sedimentary rocks; (3) salts of loesslike rocks and upper salt horizons of soils.

(3) Sulfate salts in loess-like matter. Apparently, these were transported to depositional basin from various sources. They were mixed in depositional areas of loesslike matter.

(4) The central Precaucasus area is located 200 m above sea level. It is considered an area of salt loss. The degree of eluviation is determined by local conditions, such as rock type and the geomorphological setting of the local landscape. Sulfates of the soil-loess generations essentially represent sulfate salts of the salt flux. Salt flux via ground and surface waters carries salts from the study area. This area geochemically represents the source area of matter, carried to the Precaspian region. Salts from loesslike rocks and soils are the essential components of the flux. Salts of marine deposits are of lesser importance.

(5) Carbonates in soils of the catena are represented both by newly formed pedogenic matter and inclusions of relict limestones of various fragment dimensions.

(6) Gypsum and calcite forms in the soils. Their morphological types and generations reflect the dynamics of soil development conditions.

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A GEOCHEMICAL MODEL OF THE FORMATION OF MANGANESE ORES IN THE FAMENIAN RIFT BASIN OF KAZAKHSTAN (MAJOR COMPONENTS, RARE EARTHS, AND TRACE ELEMENTS)

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Our investigation of the mineralogy and geochemistry of Mn-ores of the Famenian rift basin of Kazakhstan demonstrates that these ores are products of deposition from hydrothermal systems which evolved as a result of transgression of an epicontinental sea. Investigation of the behavior of REEs, platinoids, Ag, Au, Tl, Ge, K, Pb, Zn, and Ba allows us to conclude that the Mn-ores are a result of intracrustal subalkaline basaltic continental volcanism controlling the geochemistry of hydrothermal fluids.

The Famenian iron–manganese deposits of Kazakhstan are the largest (more than one billion tons [21]) accumulations of hydrothermal and hydrothermal-sedimentary ores in the Phanerozoic history of the Earth. Important investigations clarifying the structural and environmental settings associated with the formation of these ores and their mineral and chemical compositions have now been carried out. Investigation of metalliferous Mn- and Fe-oxyhydroxide and sulfide polymetallic sediments in the spreading zones of the ocean brings us closer to an understanding of the genesis of these deposits. Assessments of the roles of volcanism and sources of ore-forming components are especially important in this regard.

The results presented below are from an investigation into the geochemistry associated with the formation of Famenian manganese ores in Kazakhstan on the basis of contemporary concepts of hydrothermal sedimentary and hydrothermal ore formation, the main factors controlling these processes, and the rank of the Famenian manganese deposits in the hierarchy of related deposits formed over the history of the Earth.

GEOLOGICAL DATA

All of the commercially valuable iron–manganese deposits of Kazakhstan are of Famenian age and are classified as hydrothermal (volcanogenic)–sedimentary iron–manganese formations. These deposits are confined to the sublatitudinal Karakengir-Zhail'ma-Uspenska paleotrough (and the rift system of the same name) formed as a result of destruction of the epi-Caledonian Kazakhstan-Tien Shan median mass (Fig. 1). By the end of the Frasnian, this extensive massif of early consolidation was fairly stabilized and included a cover of continental crust. Beginning at the Frasnian–Famenian transition, the processes of rift formation described in detail in [14, 15] resulted in the destruction of the continental crust of the massif. Grabens, along which an epicontinental sea began to advance fairly rapidly, formed against a background of overall extension along a system of large-scale sublatitudinal cosedimentary faults. The transgression continued over the entire Famenian and reached a maximum during the Tournaisian. Within the troughs (grabens) of the Karakengir-Zhail'ma-Uspenska rift system, the thicknesses of deposits of the Famenian stage reached 500-2000 m; this was an order of magnitude greater than the thickness of the median mass over extensive areas unaffected by rifting and evolving within a quasipatform regime. Predominantly shallow-water carbonate and carbonate-terrigenous sediments accumulated within

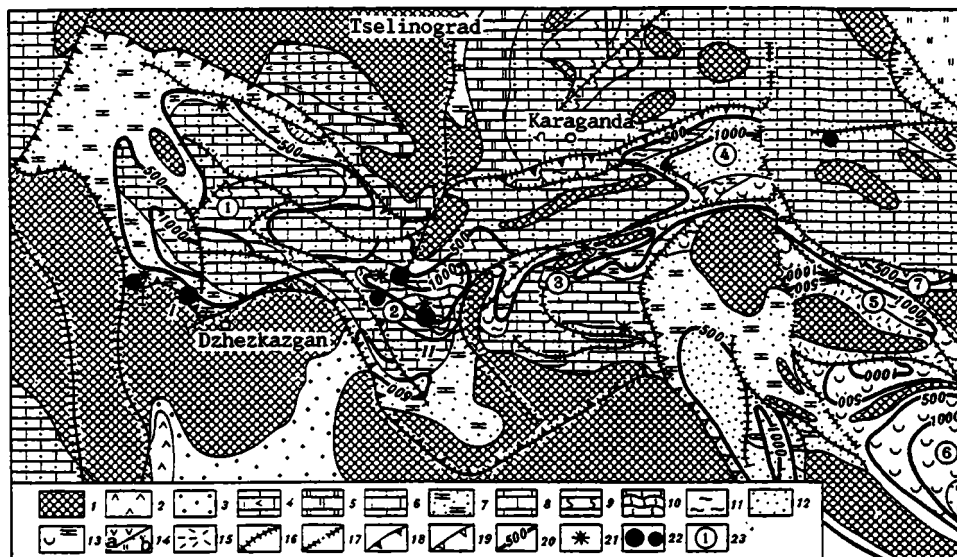


Fig. 1. Paleotectonic Map of the Famenian in Central Kazakhstan: 1) eroded areas; 2-15) geological formations and associations (2: saline, 3: clastic redbed continental, 4: carbonate-gypsiferous-clastic lagoon, 5: carbonate (predominantly dolomitic) marine, 6: calcareous marine, 7: carbonate-clastic fore-shore-marine, 8: clastic-carbonate marine, 9: redbed carbonous-laminated limestone comprising structures in upper parts of sections, 10: siliceous-carbonous-clayey-carbonate flyschoid, 11: silty-clayey, 12: clastic marine, 13: carbonate-tuffaceous-clastic flyschoid, 14: tuffaceous-clastic (a) and clastic-siliceous (b), 15: porphyreous dacitic-rhyolitic); 16-17) faults (16: cosedimentary, 17: of younger age); 18-19) boundaries (18) Karakengir-Zhail'ma-Uspenska rift system, 19: Kazakhstan-Tien Shan epi-Caledonian median mass); 20) isopachs; 21) manifestations of basaltic volcanism; 22) iron-manganese deposits; 23) individual troughs (encircled numbers): 1) Karakengir, 2) Zhail'ma, 3) Uspenska, 4) Karasor, 5) Predchingiz, 6) Tastau, 7) Degandelin; I-II Dzhezdy and Karazhal ore fields.

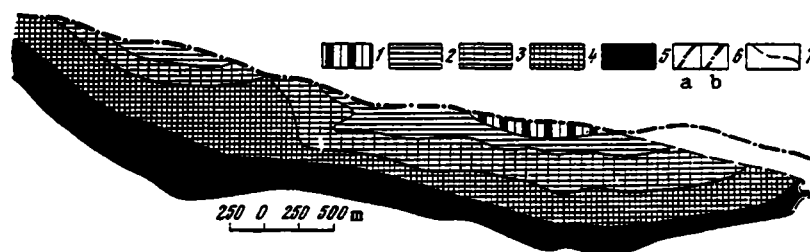


Fig. 2. Diagram of zoning in the Western Karazhal deposit (based upon [35] with additions): 1) ferruginous jasper; 2-5) ores (2: magnetite, 3: magnetite-hematite, 4: hematite, 5: manganese); 6) large cosedimentary dislocations under Tournaisian deposits (a), traced at the surface (b); 7) boundary of section of the ore deposit affected by erosion.

the Famenian marine basin of Kazakhstan; however, formation of relatively deep-water siliceous-carbonous-clayey-carbonate flyschoid formations are typical of the axial portions of the rift system.

The rift system described has a heterogeneous basement which, in many respects, controlled the depositional environments in its various parts. In the center (the Zhail'ma trough), the system was overprinted on structures of an Early Devonian volcanic edge belt. It is precisely here, within the Atasu ore district, that all of the large iron-manganese deposits and Atasu-type barite-polymetallic deposits associated with them are clustered [34, 38]. Within the rift system, there are local manifestations of basaltic volcanism coinciding with cosedimentary faults. The rocks are homogeneous in chemical composition and belong to the family of subalkaline basalts-trachybasalts, with only isolated occurrences of rocks belonging to the trachyte series. Undersaturation with respect to silica, high magnesium content, high alkalinity (with a

predominance of potassium), and elevated contents of titanium and phosphorus are typical. Accompanying potassic metasomatism is a distinctive feature of these volcanites. In general, they belong to the subalkaline potassic-sodic petrochemical series, which is characteristic of zones of continental rifting. Manifestations of such volcanism are evident in almost all the ore fields [12].

CONDITIONS OF DEPOSITION, ORE TYPES, AND MINERALOGY

The largest of the iron-manganese deposits of Kazakhstan is the Western Karazhal deposit, located in the southern portion of the Atasu district (see Fig. 1). Reserves of manganese ore in the deposit total 360 million tons; reserves of iron ore total 550 million tons [21]; 99% of the reserves are concentrated in the Glavnaya ore body, situated in siliceous-clayey nodular-laminated red limestones in the upper portion of a Famenian siliceous-carbonous-clayey-carbonate flyschoid formation. The ore body can be traced in a sublatitudinal direction for 6 km. It is comprised of iron- and manganese-ore beds which typically adjoin one another but are locally separated by ferruginous jaspers and red limestone. The northern shoulder of the ore body is comprised of predominantly iron ores; the southern shoulder is comprised of manganese ores. The latter are confined to the base and roof, but at a distance from the northern portion of the ore body; they sometimes merge in the south. Within the ore field, there is a large sublatitudinal fault zone characterized by cosedimentary movements over a substantial portion of the Famenian. This zone served as a magma conduit for basalts, which erupted beginning in the Early Famenian and continuing into the Late Famenian. The first traces of iron-manganese ore deposition appears in the Early Famenian; however, the bulk of the ores formed at the end of the Famenian, during the period when eruption of basalts terminated. Data on the zoning of the metallization (Fig. 2) and other evidence allows us to conclude that the main channelway along which ore components entered into the basin was the sublatitudinal fault zone. These space-time relationships suggest a connection between metalliferous hydrothermal fluids and Famenian volcanism. Investigation of the petrochemistry of these basalts, manifestations of alkaline, predominantly potassic metasomatism associated with the basalts, and the character of metallization suggest attributing all of these processes to a single hydrothermal-magmatic system [11].

In addition to the Western Karazhal deposit, there are three smaller deposits within the Karazhal ore field. To the east lies the Ktay ore field, to the south, the Akshagat deposit, and, to the northwest, the Zhumart ore cluster. These deposits share common geological parameters and similar genetic characteristics of iron-manganese mineralization (see Fig. 1).

The northern portion of the Atasu district includes the Ushkatyn ore field, in which, as in other deposits in this part of the district, iron-manganese and barite-polymetallic ores are widely occurring. It is precisely such objects which are classified as deposits of the Atasu type [34, 38]. Their formation took place in three main stages: 1) a hydrothermal-sedimentary stage, when the bulk of iron-manganese ores and a small portion of the polymetallic ores were deposited; 2) a hydrothermal-metasomatic stage; 3) a hydrothermal-vein stage, when primarily barite-lead-zinc ores were deposited. In the Ushkatyn III deposit, the iron-manganese and important polymetallic ore bodies are spatially separated. The pattern is different in other deposits. Thus, in the Eastern Zhayrem deposit, four iron-ore bodies with manganese are confined to horizons of red nodular limestone separated by dark-gray siliceous-clayey-carbonate rocks of flyschoid structure. The lower and middle rhythmic elements of the latter are organoclastic and finely detrital limestones, whereas, there are carbonous or pyritic, occasionally sphaleritic, rhythmites in the upper elements. Thus, iron-manganese ores and a portion of the polymetallic ores were deposited during the hydrothermal-sedimentary stage here; they alternate with one another over time.

Ratios of manganese ores to iron ores are not the same in different deposits. Some predominance of iron ores, accompanied by substantial quantities of manganese ores, is found in the Karazhal and Ktay deposits. In the Ushkatyn III and Zhumart deposits, manganese ores predominate, accompanied by subordinate quantities of hematite ores and small shows of magnetite ores.

Based upon relative predominances of essential ore minerals, we can distinguish the following types of iron and manganese ores: hematite, magnetite-hematite, magnetite, hausmannite, braunite, carbonate-silicate-hausmannite, carbonate-silicate-braunite, jacobsonite, and, in the zone of oxidation, pyrolusite-psilomelane (romanechite), cryptomelane-coronadite ores. Iron and manganese ores of the deposits under consideration are typified by a fairly wide assortment of ore-forming and admixture minerals (Fig. 3). The main ore minerals of nonhypergenetically altered ores are hematite,

In iron-ore deposits where channelways and faults of the so-called central type have been described, we find the following sequence of iron minerals: hematite + ferruginous jasper → magnetite + hematite → magnetite, chlorite + stilpnomelane → stilpnomelane + siderite → ferruginous calcite. This sequence very tentatively suggests pulsational-gradational variations in the Eh regime and relative quantities of Fe (II), Fe (III), SiO₂ and CO₂ during the process of ore formation.

The ore-mineralogical zoning described is in complete accord with data obtained during studies of hydrothermal-sedimentary deposits in axial zones of the present-day oceans and the Red Sea [5, 7, 8, 63]. Ore bodies presently forming in basins of the Red Sea are characterized by spatio-temporal relationships between iron and manganese ores similar to those found in the deposits of the Atasu district; consequently, physical-chemical characterizations of the contemporary pattern of ore deposition are, for the most part, applicable to the description of Paleozoic processes. A whole series of separate hydrothermal-magmatic systems which released hydrothermal fluids of somewhat variable compositions onto the seafloor were active under relatively deep-water conditions both in the Red Sea and in the Zhail'ma graben-trough during the Famenian. Physical-chemical conditions varied with the character of the specific locality (the composition of sediments being deposited, the geomorphology of the sea floor, etc.). Taken as a whole, this resulted in differences in ore content and composition of ores forming the deposits. At certain times, physical-chemical parameters changed during the process of ore formation in such a way that pyrite and sphalerite rhythmic units formed instead of iron-manganese ores (in the eastern Zhayrem deposit, for example).

Overall, tectonic control of sedimentation and ore formation in the Atasu district shows up in the fact that iron-manganese deposits are localized in a depositional environment characterized by carbonate-siliceous deposits (alternating with flyschoid deposits) near an abutment with different-depth facies or a steep thickness gradient outlining supra-fault scarps on the seafloor.

The data presented above allows us to distinguish a Karazhal type of iron-manganese deposit marked by an association of carbonate-siliceous deposits and hydrothermal, hydrothermal-sedimentary ore accumulation which occurred near fault zones with hydrothermal discharges.

Deposits of the Dzhezdy type occur in the western portion of the Karakengir-Uspenska rift trough (Fig. 1). They are characterized by a close association of iron-manganese-hydrothermal mineralization, hydrothermal-sedimentary mineralization and terrigenous deposits. Such deposits include the Dzhezdy, Promezhutochnoye, Nayzatas, and Zhaksy-Kotr [16, 23, 24, 26, 27, 36, 39]. The ore occurrences lie in red conglomeratic-sandstone deposits of the Early Famenian laid down in delta, beach, and coastal-plain environments at the beginning of the transgressive advance of the sea. Deposits of the Dzhezdy type (vein-sheet) include blanket ore runs with cementational mineralization and vein bodies comprised of massive ores. A spatial pattern in the distribution of vein- and sheetlike bodies as well as confinement of such bodies to the margins of tectonic depressions ("troughs-traps") bounded by consedimentary faults, has been discovered.

Primary manganese ores of deposits [24, 27, 36] in both sheet and vein-like bodies are represented by coronadite-hollandite-braunite varieties. According to data presented in [27], the main ore-forming mineral, braunite, is characterized by fine-scale heterogeneity due to syngenetic inclusions of coronadite-hollandite. The fine-grained mixture of these minerals is probably a result of recrystallization of a gel of complex composition. Hollandites include titanium-lead and zinc varieties. According to Smol'yaninova [36], cryptomelane, romanechite, and pyrolucite are the main minerals of the oxidation zone. Iron ores, primarily represented by hematite, are of negligible importance. Iron-manganese ores, represented by iron-zinc and zinc jacobsonite, are found in small quantities in the Nayzatas vein deposit. Barite is fairly widely distributed. In manganese ores, it commonly occurs in the form of irregularly shaped segregations and small crystals; more rarely, it occurs in intersecting veinlets.

Shows of subalkaline basalts coeval with the mineralization, as well as potassic metasomatism associated with such shows, are found in the Kyshtau Mountains, between the Dzhezdy and Zhaksy-Kotr deposits [12].

Thus, despite the differences noted above, manganese and iron ores of the Karazhal and Dzhezdy types show a genetic commonality based on important geological and mineralogical parameters and can be classified as hydrothermal and hydrothermal-sedimentary accumulations formed in various facial environments of a rift basin in association with continental basaltic volcanism.

TABLE 1. Chemical Compositions of Ores of Iron–manganese Deposits of the Famenian in Central Kazakhstan, Wt% (for air-dried samples)

Component	Western Karazhal		Uzhkatyn III		Uzhkatyn I		Eastern Zayrem	Dzhezdy		
	manganese (858)	iron (826)	manganese (244)	iron (66)	iron-manganese (64)	iron (30)	iron (30)	manganese (all types)	manganese bedded	manganese (vein) (1)
Mn	21,11	0,86	25,68	2,55	11,73	1,60	1,84	21,0	40,4	51,7
Fe	7,33	50,07	6,63	49,53	30,87	44,30	31,60	1,4	1,56	1,10
SiO ₂	23,15	17,17	11,76	13,79	22,38	23,70	18,09	30,0	30,0	10,9
Al ₂ O ₃	2,93	1,58	1,58	1,63	3,63	2,78	1,67(352)*	6,5	4,2	2,15
TiO ₂	0,12	0,15	0,09	0,12	0,14	0,11	0,03(105)	0,25	0,24	Traces
CaO	15,70	2,76	19,23	4,11	4,76	4,0	13,87	2,5	None	1,54
MgO	1,06	0,55	0,99	0,35	0,29	0,09	0,94(352)	1,5	Traces	0,60
K ₂ O	0,73	0,31	0,30	0,36	0,93	0,32	0,32(8)	4,0	2,77	0,87
Na ₂ O	0,84	0,24	0,36	0,39	0,25	0,17	0,21(8)	2,0	0,07	0,10
CO ₂	14,65	4,08	—	—	—	—	—	—	—	—
Ash	—	—	17,42	5,16	5,96	2,18	28,53	—	—	—
P	0,03	0,02	0,018	0,02	0,07	0,04	0,06	0,06	Traces	0,12
S _{tot}	0,06	0,21	0,13	0,21	0,15	0,11	0,73	0,14	0,27	1,26
As	0,01	0,01	0,06	0,06	0,22	0,06	0,04	—	—	—
Pb	0,14	0,06	0,16	0,04	0,53	0,15	0,05(9)	0,25	—	None
Zn	0,08	0,002	0,11	0,03	0,24	0,05	0,05(9)	—	—	—
Cu	0,009	0,033	0,003	0,003	0,01	—	0,04	—	—	—
Ge	0,00019	0,00049	0,0009	0,0015	0,0019	0,0032	0,00247	0,0007	—	—
Tl	0,00032	0,00004	0,0009	0,0003	—	—	—	0,0019	—	—
Ba	0,17	0,04	0,32	0,35	0,14	0,17	0,23	2,5	1,31	4,68
Mn/Fe	2,88	0,02	3,87	0,05	0,38	0,04	0,06	14,28	25,90	47,00
—	—	—	Rb 0,0045(46)	—	—	—	—	Rb 0,023	—	—
—	—	—	Cs 0,0047(46)	—	—	—	—	Cs 0,006	—	—
—	—	—	—	—	—	—	—	Li 0,006	—	—

Explanation. In the case of the Western Karazhal, Ushkatyn III, Ushkatyn I, and Eastern Zayrem deposits, arithmetic means based upon assays of large numbers of cluster samples obtained during exploration of these objects were used (data from A. A. Rozhnov, V. I. Shchibrik, etc.). In the case of the Dzhezdy deposit, data for the entire deposit, summarized by A. I. Nalivkina and results of assays of manganese ores in bedded and vein ore bodies by Smol'yaninova were used [36]. Numbers of samples are shown in parentheses in the table heading; numbers of samples assayed for a given element are shown given in parentheses (next to assay).

*Average for entire deposit, based upon data from A. I. Nalivkina.

TABLE 2. Abundances of Main Components and Trace Elements in Manganese Ore Deposits of Western Karazhal and Ushkatyn III

Sample number	Ca	Mn	Fe	Cu	Zn	As	Pb	Br	Sr	Y	Zr	Ba	Cr	Co	Cs	Sc	Th
Ushkatyn III deposit																	
9618-876	7,9	47,4	<0,02	<90	1800	320	<200	210	240	190	<10	630	—	—	—	—	—
9618-921	12,3	35,9	0,15	<90	73	150	380	60	1000	170	<10	240	—	—	—	—	—
9612-787	7,8	41,2	0,32	130	120	100	<200	140	280	190	<10	320	—	—	—	—	—
9621-1545	6,4	47,9	<0,02	<90	1600	200	300	28	120	200	<10	240	—	—	—	—	—
9601-III-597	3,4	48,3	<0,02	<90	1400	<30	290	22	97	210	<10	440	—	—	—	—	—
9623-413	9,4	39,4	0,73*	<90	1200	61	200	130	250	170	<10	1300	10	12	0,6	3,1	1,1
9623-428	9,9	35,1	0,22*	<90	77	<30	220	110	310	150	<10	1200	11	10	0,6	0,93	0,7
9623-617	8,3	43,2	0,44*	<90	170	110	<200	150	330	180	<10	560	6	12	0,9	1,6	0,8
9623-764	8,0	45,4	0,30*	<90	140	75	<300	170	210	200	<10	2700	11	9,8	1,0	1,3	0,7
9623-781	5,1	44,0	0,34*	<90	1500	<30	<200	200	61	220	<10	370	7,1	18	1,4	1,2	1,0
Western Karazhal deposit																	
1004-780	4,2	34,8	1,30*	<90	93	29	290	110	240	160	<10	930	51	27	3,9	4,5	1,2
1004-782	5,5	31,5	0,66*	<90	<60	36	<200	86	290	130	<10	1000	39	26	1,0	1,9	0,8
1009-767	3,8	42,7	0,10	<90	930	<30	<200	170	180	170	<10	280	—	—	—	—	—
1040a-1040	3,5	31,3	0,81*	440	230	660	35000	80	8300	180	41	2100	46	43	1,1	2,7	1,5
1043-1220	8,1	35,8	0,19	<90	120	60	650	93	430	150	<10	350	—	—	—	—	—
1040a-1210	5,1	43,9	0,53*	<90	4300	43	<200	180	130	210	<10	78	18	96	0,9	3,6	2,0
1040a-1445	11,5	32,4	0,98*	180	580	64	<200	97	2500	140	<10	360	27	35	1,1	3,2	1,2
1040a-1275	7,9	41,3	5,0*	<90	230	41	280	190	390	160	<10	1700	13	48	20	1,7	0,9
1113-826	4,1	42,3	0,05	150	230	40	<200	200	170	190	<10	170	—	—	—	—	—

Explanation. First number in sample number) hole number; second) depth, m. Sample 9618-876) hausmannite ore (hausmannite; admixture: friedelite); Sample 9618-921, braunite ore (braunite; admixture: Mn-calcite); Sample 9612-787) braunite ore (braunite; admixture: calcite); Sample 9621-1545) hausmannite ore (hausmannite; admixture: Mn-calcite); Sample 9623-781) hausmannite ore (hausmannite; admixture: calcite); samples 9623-617 and 9623-764) braunite ore (braunite; admixture: Mn-calcite, trace of galenite); Sample 1004-782) braunite ore (braunite; admixture: quartz, calcite); Sample 1109-767) hausmannite ore (hausmannite; admixture: friedelite, sphalerite); Sample 1040a-1040) braunite ore (braunite; admixture: dolomite, galenite, calcopyrite); Sample 1043-1220) braunite ore (braunite; admixture: manganocalcite); Sample 1040a-1210) hausmannite ore (hausmannite; admixture: friedelite, sphalerite); Sample 1040a-1445) braunite ore (braunite, calcite; admixture: sphalerite, quartz); Sample 1040a-1275) braunite ore (braunite; admixture: calcite); Sample 1113-826) braunite ore (braunite; admixture: Mn-calcite, friedelite).

Analyses were carried out by S. M. Lyapunov at the analytical center of the Institute of Geology, Russian Academy of Sciences for Cr, Co, Cs, Th, and Fe* using instrumental neutron-activation analysis and for other elements using X-ray fluorescence analysis. In all of the samples investigated, the content of Ti < 0.2%. Mineralogical diagnostics were carried out by means of X-ray diffractometry and mineragraphy. Contents of Ca, Mn, and Fe are given in wt%; contents of other elements are given in $n \cdot 10^{-4}$ % (ppm).

Important information concerning the main ore-forming and disseminated elements of the Famenian manganese and iron ores of Central Kazakhstan is presented in Tables 1 and 2. Consideration of these data along with the information presented above concerning mineral composition allow us to conclude that the ores under discussion are, for the most part, fairly pure manganese ($Mn/Fe = 2.9-47.0$, up to 800) and iron ($Mn/Fe = 0.02-0.06$) varieties, with subordinate quantities of mixed, iron-manganese types. While examining the material composition of the ores, it was discovered that there is a clearly expressed separation of Mn and Fe in time and in space; this is fairly typical of hydrothermal Mn- and Fe-accumulations, for example, in environments of the Galapagos rift, other spreading environments, axial areas of the ocean, and the rift zone of the Red Sea [7, 8, 63].

It is interesting that the manganese ores contain 2-3 times more carbonate than the iron ores; this manifests in correspondingly elevated concentrations of CO_2 (ash from heating), CaO , and MgO .

Phase analysis of the primary manganese ores of Ushkatyn III reveal that 68.2% of the manganese was incorporated in higher oxides, 1% was incorporated in poorly soluble silicates, and 30.8% was incorporated in carbonates and easily soluble silicates.

In most cases, iron and manganese probably arrived, along with hydrothermal solutions, onto the seafloor of the Zhail'ma basin simultaneously but in different proportions. The carbonate deposition taking place in the basin during this process had almost no effect on the composition of the iron ores. Manganese ores typically formed at appreciable distance from the source, and also formed during periods of weakened hydrothermal activity. This is one reason for the higher quantities of carbonates in manganese ores than in iron ores. Conditions under which iron and manganese precipitated simultaneously at the same site to form iron-manganese ores occurred substantially less frequently. However, reserves of such ores at Ushkatyn I are estimated to be 18 million tons.

At the Nayzatas vein deposit, which we believe to be an ore-filled channelway, iron ores are confined to the selvages of the zone and manganese ores are confined to the center.

Contents of lead and zinc in the manganese ores are 2.5-4 times higher than in the iron ores. Pb, Zn, and Ba arrived with fluids, were fixed in manganiferous sediments subsequently forming hollandite, coronadite, and cryptomelane. The somewhat elevated contents of lead and zinc in the iron-manganese ores of Ushkatyn I can be explained by the fact that rich, later galenite ores of the second hydrothermal-metasomatic stage lie at the roofs and feet of the iron-manganese ores.

Manganese ores of Dzhezdy-type deposits contain twice as much lead and substantially more barium and thallium than Karazhal-type deposits. This can probably be explained by different environmental conditions associated with ore deposition. In the marine, relatively deep-water Zhail'ma paleobasin, portions of the lead, barium, and thallium supplied from hydrothermal fluids may have been dispersed. Under the surficial conditions associated with small, freshwater ponds in the Dzhezdy-Zhaksy Kotr region, discharge of hydrothermal fluids, accompanied by the formation of vein and sheet manganese ore bodies, took place with an abrupt change in physical-chemical conditions. In the sheet bodies, we find much more cryptomelane, hollandite, and locally, individual segregations of barite.

Thus, the compositions of hydrothermal fluids are reflected to a greater degree in the compositions of ores in Dzhezdy-deposits than in ores of the Karazhal type.

Relatively high concentrations of Tl ($2-128$, averages of $3-19 \cdot 10^{-4}\%$) and comparatively low concentrations of Ge ($1-55$, averages of $2-9 \cdot 10^{-4}\%$) are characteristic features of Mn-ores in the deposits being described (Table 1). This was noted in [18-20]. It should be emphasized that high contents of Ge occur in Fe-ores ($1-160$, $5-32 \cdot 10^{-4}\%$). When interpreting these data, it is necessary to keep in mind that the abundances ($n \cdot 10^{-4}\%$) of Tl and Ge in clay rocks of the Earth's crust [62] equal 1.4 and 1.6 respectively. Comparison of these values reveals that Famenian Mn-ores of Central Kazakhstan are enriched in Tl, averaging 2.3-13.6 times more than in clays of the lithosphere (in which quantities of trace elements are the highest among sedimentary rocks) and Ge, averaging 1.25-5.62 times more. In Fe-ores, the content of Tl is substantially less than in clays of the Earth's crust ($0.4-3.0 \cdot 10^{-4}\%$); whereas, the relative accumulation of Ge in these ores is fairly high (3.12-20.0 times more than in the crust). The differences noted in the behaviors of Tl and Ge are controlled by differences in crystal-chemical affinities of ions of these elements for Mn and Fe, which result in their sorptive accumulation during precipitation of oxyhydroxide phases of Mn and Fe in hydrothermal systems [28].

The abundance of thallium (as well as lead) in manganese ores of deposits of the Dzhezdy type is several times (2-6) greater than in ores of the Karazhal type. Here, the quantity of thallium in blanket bodies is clearly a function of

TABLE 3. Abundances of Rare-Earth Elements in Manganese Ores of Western Karazhal and Ushkatyn III, $n \cdot 10^{-4}\%$ (for air-dried samples)

Sample number	Component											
	9623-413	9623-428	9623-617	9623-764	9623-781	1004-780	1004-782	1040a-1340	1040a-1210	1040a-1445	1040a-1275	mean (n = 11)
	1	2	3	4	5	6	7	8	9	10	11	12
La	10	3,3	10	3,2	3,1	11	9,1	29	40	29	6,7	14,04
Ce	6,7	3,8	6,7	2,8	4,3	17	14	10	9,3	21	8,1	17,04
Sm	1,7	0,5	1,5	0,53	0,61	2,8	1,7	3,8	7,9	3,6	1,2	2,35
Eu	0,40	0,14	0,30	0,097	0,11	0,49	0,31	1,3	3,2	1,4	0,31	0,732
Tb	0,30	0,092	0,24	0,075	0,076	0,50	0,25	0,68	1,1	0,63	0,20	0,377
Yb	0,72	0,025	0,64	0,33	0,22	1,5	0,94	1,6	2,0	1,70	0,60	0,934
Lu	0,093	0,035	0,093	0,042	0,038	0,19	0,17	0,22	0,29	0,23	0,096	0,136
Σ REEs	19,913	7,892	19,473	7,074	8,454	33,48	26,47	46,60	147,49	57,56	17,206	35,609
$\Sigma(\text{La} - \text{Sm})/\Sigma(\text{Eu} - \text{Lu})$	12,16	26,03	14,30	12,00	18,04	11,49	14,85	11,26	21,38	13,53	13,27	15,34
La/Yb	13,89	132,00	15,62	9,70	14,09	7,33	9,68	18,12	20,00	17,06	11,17	15,03
La/Sm	5,88	6,60	6,67	6,04	5,08	3,93	5,35	7,63	5,06	8,05	5,58	5,97
Ce/Sm	3,94	7,60	4,47	5,28	7,05	6,07	8,23	2,63	11,77	5,83	6,75	7,25
Eu/Sm	0,23	0,28	0,20	0,18	0,18	0,17	0,18	0,34	0,40	0,39	0,26	0,31

Explanation. 1. For description of samples, see explanation beneath Table 2. Determinations were carried out using instrumental neutron-activation analysis at the analytical center of the Institute of Geology of the Russian Academy of Sciences, by S. A. Lyapunova.

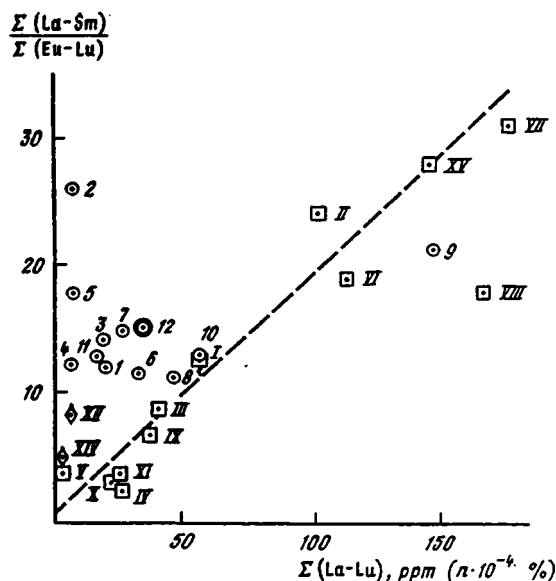


Fig. 4. Correlations between $\Sigma(\text{La} - \text{Lu})$ and $\Sigma(\text{La} - \text{Sm})/\Sigma(\text{Eu} - \text{Lu})$ in manganese ores of the deposits of Central Kazakhstan and main rock types in crust (sample numbers in this and subsequent figures correspond to the numbering in Tables 3 and 4).

distance to the ore-channeling vein zone. In the Dzhezdy deposit, according to the findings of A. I. Nalivkina, maximum contents of thallium ($10\text{--}60 \cdot 10^{-4}\%$) and lead ($0.1\text{--}0.44\%$) occur just north of the ore-channeling Dzhezdy and Karasakpaysk faults. In one case, $128 \cdot 10^{-4}\%$ Tl was found. In a sheet of the Promezhutochnoye deposit located at a distance from the vein zones, the average content of thallium equals $6.1 \cdot 10^{-4}\%$; the abundance of thallium in manganese ores of the vein zone of the Nayzatas deposit is $29.0 \cdot 10^{-4}\%$.

The content of thallium in manganese ores of Western Karazhal averages $3.2 \cdot 10^{-4}\%$, with variations in individual cluster samples ranging from <0.5 to $56 \cdot 10^{-4}\%$; at Ushkatyn III, the content of thallium equals $9 \cdot 10^{-4}\%$ ($2\text{--}100$) $\cdot 10^{-4}\%$.

It should be noted that the content of thallium is very high in globular pyrite-marcasites in corresponding rhythmites formed, as in the case of iron-manganese ores, during the first hydrothermal-sedimentary stage in deposits of the Atasu type; the abundance of thallium is $90\text{--}120 \cdot 10^{-4}\%$ at Ushkatyn III, $120 \cdot 10^{-4}\%$ at Ushkatyn I, and $150\text{--}60 \cdot 10^{-4}\%$ at Zhayrem [32]. In Western Karazhal, with an average thallium content in iron ores equalling $0.4 \cdot 10^{-4}\%$, there are areas of hematite ore containing a disseminated impregnation of pyrite. The content of thallium in the latter equals $15.6 \cdot 10^{-4}\%$.

Maksimov [29] first discovered high contents of germanium in the iron-manganese deposits of Central Kazakhstan. Grigor'ev made a study of this problem, with special reference to Western Karazhal [22]. He found that magnetite is the main mineral-concentrator of germanium, with magnetites of siderite-magnetite ($56 \cdot 10^{-4}\%$) and hematite-magnetite ($44 \cdot 10^{-4}\%$) ores characterized by the greatest concentrations. Subsequent detailed investigations (A. A. Rozhnov, V. I. Shchibrik, and others) during supplementary exploration of the deposit revealed that maximum contents of germanium (up to $195 \cdot 10^{-4}\%$) occur in cryptocrystalline magnetite and metacrystals of magnetite (up to $134 \cdot 10^{-4}\%$)

TABLE 4. Abundances of REEs in Subdivisions and Rocks of the Crust and Hydrothermal Iron–Manganese Deposits,
 $n \cdot 10^{-4}$ (ppm)

Component	I. Continental crust	II. Upper continental crust [59]	III. Lower continental crust [59]	IV. Oceanic crust (basaltic portion) [59]	V. Primitive mantle (contemporary mantle + crust) (59)	VI. North American clay slate [50]	VII. Alkali basalts [3]	VIII. Granites [4]	IX. Continental tholeiites [3]	X. Tholeiites of oceanic ridges [3]	XI. Tholeiites of axial zone of Red Sea [1]	XII. Hydrothermal Mn-oxyhydroxides [53, 63]	XIII. Hydrothermal braunite [45]	XIV. Green hydrothermal clay [53, 63]	XV. Subalkalic basalts of Afar [55]
La	16	30	11	3,7	0,551	32	59	56	7,7	3,46	5,9	2,62	1,72	0,74	49,9
Ce	33	64	23	11,5	1,436	70	105	92	20,3	10,3	10,4	3,5	5,0	1,47	84
Sm	3,5	4,5	3,17	3,3	0,347	5,7	7,1	10,0	4,1	3,49	3,2	0,78	0,68	0,174	6,07
Eu	1,1	0,88	1,17	1,3	0,131	1,24	2,0	1,6	1,3	1,26	1,1	0,167	0,173	0,107	2,03
Tb	0,6	0,64	0,59	0,87	0,087	0,85	1,13	1,6	0,77	0,86	0,66	0,141	—	0,074	0,70
Yb	2,2	2,2	2,2	5,1	0,372	3,1	2,0	4,0	2,45	3,2	3,3	0,437	0,23	0,213	1,76
Lu	0,30	0,32	0,29	0,56	0,057	0,48	0,3	1,2	0,4	0,49	0,45	0,063	0,029	0,062	0,330
Σ REEs	56,7	102,54	41,42	26,33	2,98	113,37	176,53	166,4	37,02	23,06	25,01	7,708	7,832	2,84	144,79
$\Sigma(\text{La} - \text{Sm}) / \Sigma(\text{Eu} - \text{Lu})$	12,5	24,3	8,7	2,36	3,60	18,99	31,51	18,81	6,52	2,97	3,54	8,54	—	5,23	29
La/Yb	7,27	13,64	5,00	0,75	1,48	10,32	29,5	14,00	3,14	1,08	1,79	5,99	7,48	3,47	28,3
La/Sm	4,57	6,67	3,47	1,12	1,59	5,61	8,31	5,6	1,88	0,97	1,84	3,36	2,53	4,25	8,2
Ce/Sm	9,43	14,22	7,25	3,48	4,14	12,28	14,79	9,2	4,95	2,95	3,25	4,49	7,35	8,45	13,8
Eu/Sm	0,31	0,19	0,37	0,39	0,38	0,22	0,28	0,16	0,32	0,36	0,34	0,21	0,25	0,61	0,33

from magnetite-hematite ores; such concentrations are found only in ores in the central and eastern parts of the deposit, the parts of the deposit closest to the channelway (see Fig. 2) and subjected to the least dynamic metamorphism. As a result, iron-germanium ores containing $\text{Ge} > 5 \cdot 10^{-4}\%$ were discovered in the deposit. Their reserves constitute 3/5 of all iron ores in the deposit [21]. Higher contents of germanium occur in iron ores of Ushkatyn I and Eastern Zhayrem (see Table 1). In monomineralic samples of the latter, magnetite contains up to $300 \cdot 10^{-4}\%$ Ge; hematite-magnetite ores of the Nayzatas deposit contain $8.6 \cdot 10^{-4}\%$ Ge.

It is important to emphasize again that high contents of thallium in manganese ores and high contents of germanium in iron ores are characteristic features of all deposits of the formation being described over the entire extent (more than 700 km) of the Karakengir-Zhail'ma-Uspenska rift system.

Data on the behaviors of rare-earth elements (REEs) during formation of deposits is very useful for determining the genetic nature of Mn-ores in deposits of Central Kazakhstan.

Determinations of REEs were carried out for samples of manganese ores from deposits of the Karazhal type (see Table 2 and Table 3). At Ushkatyn III, ore bodies 4-6 and 9 were sampled in the area of Pedstiyevskiy; Ore Body 3 was sampled in the center of the deposit (Hole 1004) and Ore Body 4 was sampled in the extreme west (Hole 1040a). Table 2 shows that, although abundances of Mn- and Fe-ores in Western Karazhal are very similar to abundances in Western Ushkatyn, the ores of Western Karazhal contain 3-4 times more Cr, Co, and REEs than ores of Ushkatyn III (9, 12, and $12 \cdot 10^{-4}\%$ at Ushkatyn III and 32, 46, and $55 \cdot 10^{-4}\%$ in Western Karazhal). Especially among six samplings of Western Karazhal, we find samples 1040a-1340, 1040a-1210, and 1040a-1445 in which the quantities of Pb, Zn, Ba, and Sr are greater by an order of magnitude or more. Mineralogical data indicates that galenite, sphalerite, and chalcopyrite are found in almost only these three samples, suggesting a superimposition of metallization on the iron-manganese ores during these intervals of the second (hydrothermal-metasomatic) stage. Maximum quantities of REEs are found in precisely these samples ($46.6\text{--}147.49 \cdot 10^{-4}\%$).

Comparison of total accumulation of REEs [$\Sigma(\text{La} - \text{Lu})$] and degree of fractionation of light and heavy REEs [$\Sigma(\text{La} - \text{Sm})/\Sigma(\text{Eu} - \text{Lu})$] in the crust and in its main subdivisions (Table 4 and Fig. 4) shows a distinct trend toward increases in these parameters with increasing transformation of oceanic crust ($\Sigma(\text{La} - \text{Lu}) = 26.33 \cdot 10^{-4}\%$; $\Sigma(\text{La} - \text{Sm})/\Sigma(\text{Eu} - \text{Lu}) = 2.36$) into upper continental crust ($\Sigma(\text{La} - \text{Lu}) = 102.54 \cdot 10^{-4}\%$; $\Sigma(\text{La} - \text{Sm})/\Sigma(\text{Eu} - \text{Lu}) = 24.3$). It also shows a clear difference between tholeiites of mid-oceanic ridges and axial zones of the Red Sea, on the one hand, and subalkaline basalts, in particular subalkaline basalts of the Afar region, on the other. It should be noted that ratios of these parameters for subalkaline basalts are similar to those for North American clays and clay slates.

Mn-hydrothermal sediments of the axial zones of the ocean show a distinct grouping on this diagram, resembling tholeiites of oceanic ridges in terms of total REEs and ratio of light to heavy REEs. With respect to the former, Karazhal-type manganese ores show a trend similar to that from mid-ocean-ridge tholeiites to subalkaline basalts of continental rift zones; although the trend is substantially weaker in expression.

The significance of the quantity Eu/Sm as an indicator of the fraction of components with hydrothermal origins in Mn-Fe-sediments, nodules, and crusts in the ocean was demonstrated in earlier reports [10, 64]. It was shown that Eu/Sm equals 0.18-0.25 in Mn-Fe-oxyhydroxide accumulations formed predominantly from components of terrestrial runoff; this is similar to the ratio for upper continental crust (0.19; see Table 4). In the majority of Mn-Fe-metalliferous sediments, moreover, crusts, and nodules formed with substantial participation of hydrothermal components, $\text{Eu}/\text{Sm} > 0.2$; this matches the ratio in tholeiitic basalts of the ocean (0.36; see Table 4). Our conclusion is confirmed by an investigation of the manganese ores of Central Kazakhstan (Fig. 5, see Tables 3 and 4). Analysis of the diagram showing the correlations of $\Sigma(\text{La} - \text{Lu})$ and Eu/Sm shows that, for the observed scatter of points corresponding to the Mn-ores under consideration, these values do not exceed those subalkaline basalts, at least, primitive, poorly differentiated basalts: $\text{Eu}/\text{Sm} = 0.17\text{--}0.40$ (an average of 0.31) for relatively low values of $\Sigma(\text{La} - \text{Lu})$ (an average of 35.609).

On a $\Sigma(\text{La} - \text{Lu}) - \text{La}/\text{Sm}$ diagram illustrating the relationship between accumulation of REEs and a measure of fractionation of light and transitional (intermediate) fractions of REEs, there is a clearly expressed trend reflecting the direct relationship between these parameters at the transition from oceanic crust to continental.

Relationships between tholeiites of mid-oceanic ridges and the Red Sea, on the one hand, and subalkaline basalts of continental rift zones, Mn-hydrothermal sediments of axial zones of the ocean, and also ophiolitic zones and hydrothermal-sedimentary Mn-ores of Central Kazakhstan, on the other, stand out even more distinctly on this diagram. In [12] it is shown that Famenian subalkaline olivine basalts of the Karakengir-Zhail'ma-Uspenska rift zone especially resemble

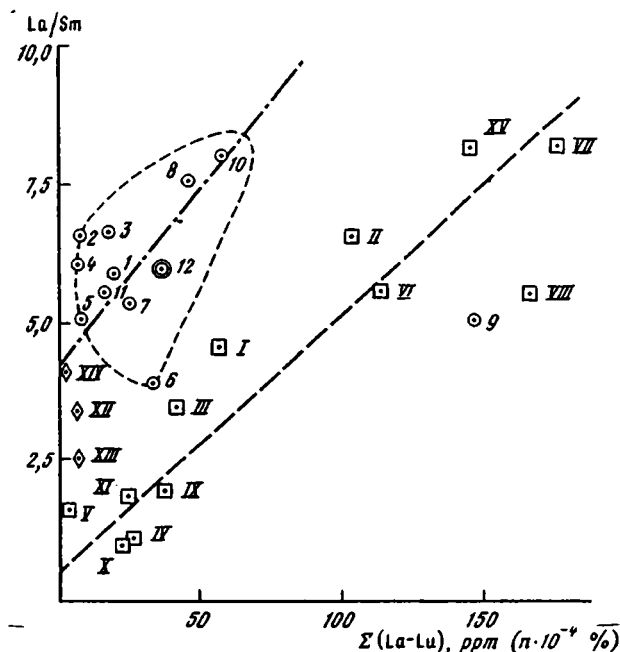


Fig. 5. Relationship between $\Sigma(\text{La} - \text{Lu})$ and La/Sm in manganese ore deposits of Central Kazakhstan and main rock types in crust.

subalkaline basalts of the Afar region with respect to petrochemical and geochemical characteristics. This allows us to assume similar contents of REEs in these basalts. Proceeding on this assumption, our diagrams (see Figs. 4-6) lead us to conclude that there is a kinship between the Mn-ores of Kazakhstan we are discussing and the basaltoids which accompany them; they are members of a single hydrothermal-magmatic association.

However, not only the depth at which subalkaline basalts melted out (restricted by the appreciable thickness of crust) but also the very passage of the basaltic melt and the fluid accompanying it through this thick crust, affected the geochemical characteristics of these ores. Partial melt-outs of crustal material, resulting in limited occurrences of trachytes and enrichment of the fluid with K, Pb, Zn, Ba, Tl, and a number of other elements, took place along this pathway (or in intervening chambers).

Precisely these crustal chambers at intermediate depth probably served as the source of Ba-polymetallic ores in the second stage of Atasu-type deposits.

Table 5 shows abundances of elements of the platinum group (EPG), gold, and silver in manganese ores of the Karazhal type. The following conclusions can be drawn from a consideration of these data.

Abundances of platinum-group elements in almost all samples investigated were less than the abundances of these metals in basic rocks of the Earth's crust ($\text{Pt}, 1 \cdot 10^{-5}\%$ [17]) and in sediments of the ocean ($\text{Pt} 3.5 \cdot 10^{-7}\%$ [2]). In metalliferous sediments and in oceanic Mn-Fe-oxyhydroxide crusts closely associated with submarine volcanism, the Ogasawara submarine plateau in the Western Pacific, for example, the abundance of Pt equals $(0.19-0.76) \cdot 10^{-4}\%$ [60]; in massive sulfide ores from the 21°N region of the East Pacific Rise, concentrations of up to 1% have been found [51]. In other words, deposits which are products of hydrothermal activity associated with basic and ultrabasic volcanism of oceanic crust are among the richest types of EPG accumulations [54]. The low abundances of Pt and other EPG in the Mn-ores under consideration supports the idea that the deposits were associated with subalkaline continental basaltoid volcanism.

In contrast to the situation with respect to platinoids, substantial enrichment of Au and Ag are found in the Mn-ores of Central Kazakhstan (see Table 5). If we assume that the average concentration of Au is $1 \cdot 10^{-7}\%$ in basic rocks and the average concentration of Ag is $1 \cdot 10^{-5}\%$ [17], then the ores under consideration average 16-fold and 122-fold enrichments of these elements respectively. Such concentrations of Au and Ag substantially exceed accumulations of these metals in Mn-Fe-oxyhydroxide phases in the ocean. The similarities in the distribution patterns of these elements may indicate an important role for rock in the upper reaches of continental crust as a source of ore-forming components.

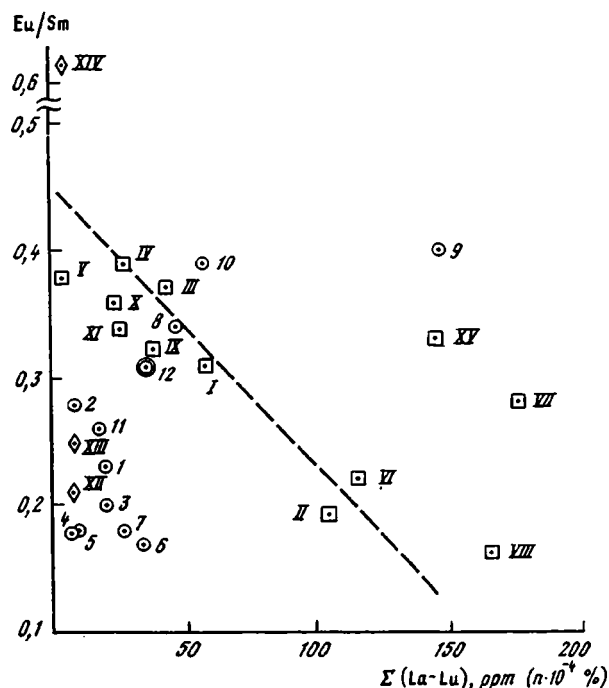


Fig. 6. Relationship between $\Sigma(\text{La} - \text{Lu})$ and Eu/Sm in manganese ores in deposits of Central Kazakhstan and main types of Earth's crust.

TABLE 5. Abundances of Elements of the Platinum Group, Gold, and Silver in Manganese Ores of the Deposits of Western Karazhal and Ushkatyn III, $n \cdot 10^{-4}\%$ (for air-dried samples)

Sample number	Ru	Au	Ag
1004-780	<0,004	0,018	14,22
1004-782	0,004	0,014	12,51
1040a-1340	<0,004	0,016	6,82
1040a-1210	0,007	0,013	17,06
1040a-1275	<0,004	0,013	21,04
1040a-1445	<0,004	0,012	19,91
9623-413,0	0,004	0,014	9,10
9623-428	<0,004	0,014	3,41
9623-697	0,004	0,020	5,12
9623-764	0,004	0,022	10,81
9623-781	0,007	0,018	14,78
Average (n = 11)	<0,004	0,012-0,022 (0,016)	3,41-21,04 (12,25)

Explanation. Descriptions of samples are provided in explanation beneath Table 2. Assays were carried out at the analytical laboratory of the Central Scientific-Research Institute of Geological Exploration, Moscow University, USSR: gold and silver) using methods of flame-atomic-emission, kinetic, and atomic absorption analysis; platinum, palladium, and rhodium were assayed by means of the cerium-arsenite indicator reaction. In all of the samples assayed, $\text{Pt} < 0.003$; $\text{Pb} < 0.0015$; $\text{Rh} < 0.002$; $\text{Os} < 0.004$; $\text{Ir} < 0.1$.

Thus, the data presented on the distribution of major components and trace elements, in particular, rare earths, platinoids, gold, and silver (see Tables 1-5), in Famenian hydrothermal-sedimentary manganese ores of Kazakhstan

definitely indicate that the ores are derived from the activity of hydrothermal-magmatic systems arising during rifting, during the destruction of continental crust, and during manifestations of subalkaline basaltic volcanism accompanied by alkaline (potassic) metasomatism.

GENETIC MODEL

Current information on the geochemistry of the formation of Mn-Fe-oxyhydroxide and polymetallic hydrothermal deposits in axial zones of the ocean [40, 48, 63] has been a substantial aid in the formulation of hypotheses concerning processes of this type which may have occurred in paleobasins. Especially notable progress has been achieved as a result of direct observations and quantitative measurements, as well as by evaluation of factors which may be critical to the genetic model.

In contemporary ocean basins, it is primarily seawater which plays the role of the hydrothermal fluid; under conditions of a hydrothermal system at high temperature and pressure, seawater is transformed into a chloride solution distinguished by low pH (3.0-3.5) and low Eh, as well as millimolar concentrations of H_2S , Fe, and Mn. Such solutions are depleted of Mg^{2+} and sulfate ion, and are variably enriched in K and Ca, as well as Li, Rb, and Be relative to the original seawater. The ionic strengths of such solutions can vary from 60 to 130% of values characteristic of seawater [48, 65]. During convective circulation of such corrosive solutions in a hydrothermal system, selective extraction and leaching of Mn, Fe, Pb, Zn, Cu, As, REEs, and other components from the enclosing, primarily basaltic rocks takes place.

In contrast to geological and environment conditions found in the ocean, formation of the Famenian Mn- and Fe-ores of Central Kazakhstan was characterized by a number of features specific to this region.

Hydrothermal processes linked to iron-manganese mineralization were ongoing in the Karakengir-Zhail'ma-Uspenska rift trough formed during the Late Devonian as a result of destruction of continental crust of the Kazakhstan-Tien-Shan epi-Caledonian massif. The rifting processes were accompanied by advance and transgression of an epicontinental sea, as well as locally manifested subalkaline basaltic volcanism.

The deposits of Central Kazakhstan which we are discussing formed under various environmental conditions. Ferromanganese ores of the Karazhal type were deposited under relatively deep-water conditions of a Famenian sea, while ores of the Dzhezdy type were deposited in nearshore-continental environments of beaches, deltas, and alluvial plains. Although the ore material brought by hydrothermal springs was deposited in several different physical-chemical environments, the mineralogical-geochemical compositions of the ores in both types of deposits under consideration are so similar that their sources can be considered identical. Elevated contents of Pb, Ba, Tl, Ag, and (to some degree) Au, as well as low contents of EPG, are characteristic features of the geochemistry of Famenian hydrothermal-sedimentary manganese ores; elevated contents of Ge are characteristic of iron ores. By taking this into account and also by analyzing the distribution pattern of REEs, we arrived at the conclusion that subalkaline basalts and the fluids accompanying them, which were enriched with a whole series of elements during passage through the thick continental crust, played a definite role in the hydrothermal-magmatic systems-sources of ore matter. The role of the continental crust as a source of ore elements especially increased during the formation of the hydrothermal-metasomatic barite-polymetallic ores of Stage II in the formation of Atasu-type deposits.

Metallogenic analysis shows [13] that maximum ore content is characteristic of that portion of the Karakengir-Zhail'ma-Uspenska rift system which is overprinted on an Early Devonian marginal volcanic belt (the Atasu district). On the one hand, conditions were very favorable for concentration of metallization within the Zhail'ma trough; on the other hand, violent, earlier volcanic activity took place within the belt from the Early Devonian through Frasnian, marked by formation of a large number of crustal magma chambers, probably reflected in the widespread potassic metasomatism which accompanied the Famenian basaltic volcanism and in formation of unique barite-polymetallic deposits along with iron-manganese deposits.

GENETICALLY RELATED DEPOSITS OVER THE COURSE OF GEOLOGICAL HISTORY

The Famenian rifting associated with the formation of manganese deposits in Kazakhstan was part of a global process [14, 15]. Episodes of global continental rifting were accompanied by phases of overall heating of the Earth following unification of continents into supercontinents and, in turn, foreshadowing major phases of opening of new oceans as a result of rapid propagation of spreading axes [33].

Pleistocene–Holocene rifting, leading to the formation of the East-African rift system and the rift of the Red Sea, was accompanied by formation of small iron–manganese and barite-polymetallic deposits on land, as well as metalliferous sediments in the Red Sea. Whereas ore accumulation in deep-water basins of the Red Sea [6-8] can be compared to phenomena now taking place in the spreading zones of the ocean [40, 48, 63, 65] and accompanied by eruptions of low-potassium tholeiites, iron–manganese and barite-polymetallic deposits [44, 46] are associated with subalkaline basalt complexes. The geological conditions associated with formation of deposits on land and also the geochemical characteristics of such deposits are similar in many ways to those of Dzhezdy-deposits in Kazakhstan.

The development of the East-Pacific rift belt at the transition from the intracontinental rift zone of the Gulf of California on the North American continent resulted in the formation of the broad Basin and Range Province opening fanlike toward the north and manifesting as numerous alternating narrow grabens, horsts, and blocks dipping in the same direction [30]. During the Miocene, stratiform deposits of Mn-ores (reserves >7 million tons) genetically related to Famennian Mn-deposits of the Dzhezdy type in Kazakhstan formed among sedimentary and volcanic rocks in the southern portion of the Basin and Range Province. These stratiform deposits are localized in two regions: 1) the Three Kids-Virgin River, southern Nevada; 2) the Artillery Mountains in the western portion of central Arizona [52]. Mn-mineralization is localized in lacustrine, alluvial, and fluvial deposits, as well as limestones. In the deposits of southern Nevada, Mn-ores are represented by todorokite and coronadite; in central Arizona, Mn-ores are represented by coronadite-hollandite and cryptomelane and are distinguished by high concentrations of Pb (up to 14%), Ba (up to 5%), As (up to 0.5%), and U (up to $40 \cdot 10^{-4}\%$). The modes of occurrence, compositions, and structural characteristics of the Mn-deposits indicates that manganese precipitated from relatively low-temperature hydrothermal solutions at contacts with unconsolidated clastic sediments on the lake floors or under the floors of stratified saline lakes. Primordial values of $^{86}\text{Sr}/^{87}\text{Sr}$ (0.71005–0.71666) for the enclosing evaporites and limestones would suggest lacustrine environments. In the opinion of the authors cited, Pb-isotope ratios in Mn-ores suggests that the source of Mn and other metals was Proterozoic and Mesozoic basement rocks. Processes of extension, volcanism, and manganese mineralization proceeded simultaneously. The proximity of the detachment surface to magma chambers of active volcanism resulted in the development of large hydrothermal convection cells. Faults bordering the tensional extension may have served as conduits for replenishing the saline basin with water and may have served as circulation paths for the entry of heated hydrothermal solutions.

The formation of the Mesozoic rift system in the territory of the Great Atlas was a special case, beginning in the Triassic, of a immense rifting process finally resulting in the creation of the central portion of the future Atlantic Ocean [31, 58]. A large group of hydrothermal(volcanogenic)-sedimentary deposits of Jurassic and Cretaceous age formed within this structure [58].

If we tentatively assume that the hypogene karst processes were overprinted and limit our investigation of origin [61] to an analysis of available data, the primary ratios of Mn-oxide ores in the region of the Imini and Tasdremt deposits of the Senomanian–Tournian of Morocco, we can compare these processes with hydrothermal mineralization of the Dzhezdy type [9, 56, 57]. In both regions, manganese ores are rich in Pb (up to 3.3%), Ba (up to 4.5%), Zn (up to 0.1755%), Y (up to 0.085%) and other heavy metals, which are present in the forms of coronadite, hollandite, and other oxide minerals. Manganese and polymetallic hydrothermal mineralization also occurs in the form of small deposits and ore shows in the lower lying deposits of the Liassic and in volcanogenic–sedimentary formations of the porphyritic series in the Precambrian folded basement of this region.

In Southern China and Northern Vietnam, globally occurring Famennian rifting caused the formation of manganese deposits and accompanying polymetallic deposits. Hydrothermal-sedimentary manganese deposits are confined to a network of rift troughs located at the southern margin of the South-China metaplatform, primarily on post-Caledonian folded basement. In the Xialei deposit, manganese ores, represented by rhodonite, rhodochrosite, manganocalcite, and other minerals, contain elevated quantities of Cu, Pb, Zn, Ag, Co, and Ni [66, 67]. Hematite has been found in the ores. The content of REEs in the ores correlates with the content of Mn. Abundances and distribution patterns of REEs (chondrite-normalized) are the same as those for bentonite deposits; this suggests a source in the upper crust. Isotopes of S and C suggest an endogenous source of ore elements. Famennian deposits enclosing the ore beds include carbonate-pyritaceous-siliceous rocks, banded limestones, clayey-siliceous, and siliceous rocks. Coeval volcanogenic include trachytes, basalts, and their tuffs. A special feature of this group of hydrothermal-sedimentary iron–manganese and stratiform polymetallic deposits of Southern China is the presence of deposits of Sb and Sn among them. Typically, Sinian, Permian, and Triassic episodes of predominantly sedimentary manganese accumulation are clearly identifiable, in addition to a Famennian manganese-ore episode.

Not much can be said concerning rifting processes during the Early Proterozoic, although the data presented in [42] indicates that substantial eruptions of basalt and formation of manganese deposits took place at the end of the formation of the Transvaal supergroup (the Postmasburg group) at the boundary between the platform (the Kaapval craton) and the basin bordering it on the west, due to tectonic activation. These accumulations of manganese ores in the Hatazel formation, the Kalahari deposit (Griqualand West, Cape Province, South Africa), are world-class. Assuming that 5026.3 million tons of Mn are concentrated in the ores of Kalahari Province [47, 49], this amounts to 78.8% of world-wide reserves of manganese ore on land from the Archean to the Holocene. Manganese runs in this region are interfingered with iron ore runs and alternate upward along the section with dolomite. Mn-ore-bearing deposits accumulated in a basin which was primarily supplied with ore components from hydrothermal springs associated with a thick series of pillow lava. Mn-ores are represented by braunite, kutnahorite and manganese calcite [41, 43]. Despite the colossal scales of accumulation of manganese ores noted above, the substantial portion of the Mn supplied by hydrothermal fluids to this Early Proterozoic sedimentation basin nevertheless binded to a very limited extent with low-valence (braunite) oxides and diagenetic carbonate ores dispersed in the water column, since the abundance of oxygen in the atmosphere at that time was approximately one hundredth of its present value.

The evidence presented indicates that large-scale volcanogenic-sedimentary manganese deposits on the continents were created as a result of destruction of consolidated lithospheric crust, primarily due to rifting. If the use of indicator deposits [37] to analyze the metallogeny of rift zones is valid, the iron-manganese deposits described, with their characteristic geochemical features, frequently accompanied by barite-polymetallic mineralization, can serve as reliable indicators of this type of geodynamic regime.

The Famenian iron-manganese ores of Central Kazakhstan were a result of hydrothermal-sedimentary processes which evolved in the Karakengir-Zhail'ma-Uspenska rift trough, created as a result of destruction of the epi-Caledonian Kazakhstan-Tien Shan median mass. Rifting was accompanied by transgressions of an epicontinental sea and subalkaline basaltic volcanism. Mn- and Fe-ores of Karazhal-type deposits, amassed in oxyhydroxide forms, were deposited in relatively deep-water environments of the Famenian sea, whereas, accumulation of similar ores of the Dzhezdy type took place in environments of coastal shoals and deltaic alluvial plains.

The overall geochemical characterization of the manganese ores of Kazakhstan as products of thermal-magmatic systems allows us to propose that the compositions of these systems were determined, on the one hand, by the depth at which subalkaline basalts melted out (this depth, as well as other factors, being dependent on the presence of a substantial thickness of continental crust) and, on the other hand, by the path of the basaltic melt and accompanying fluid through this thick crust. Melting out of crustal material, resulting in minor occurrences of trachytes and enrichment of the fluid in K, Pb, Zn, Ba, Ag, Tl (in part, Au), and a number of other elements, probably took place along this path (or in chambers at intermediate depths). It is precisely these intervening chambers which may have served as the source of Ba-polymetallic ores for the second stage in deposits of the Atasu type. It is therefore apparent that those regions of the rift system which were overprinted on the Early Devonian marginal volcanic belt are distinguished by the greatest ore content.

In geological history, formation of manganese ores of this type have been noted from the Early Proterozoic to the Holocene.

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POST-RIFT SEDIMENTOGENESIS OF THE CARBONIFEROUS IN THE NORTHERN VERKHOFAN REGION

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We report new information on the structure and genetic features of the Carboniferous in the Orgulan structural-facies zone of the Northern Verkhofan region. We propose a model of the evolution of a marine sedimentation basin in specific conditions where the rifting geotectonic setting gives way to a miogeosynclinal regime. We emphasize the need for further specific definition of the lithologic indicators of early geosynclinal paleodynamics. We also discuss general problems of the evolution of sedimentogenesis in geologic history.

Recent geologic exploration in the Verkhofan folded system has provided new sound arguments to support the theory that the sedimentary basin with miogeosynclinal tectonics which existed in this area during the Early Paleozoic and Mesozoic was formed on an activated platformal margin [29, 30, 39]. The beginning of its foundation is dated by the Middle Visean [7, 12]. Its prehistory encompasses prolonged periods of destructive transformations of the continental crust of the North Asian craton, which occurred by way of multiphase rifting during the Riphean, Vendian, and Middle Paleozoic [5, 9, 14, 16, 17, 34, 44].

Our attention was attracted by geologic events that occurred immediately after rifting tectonics gave way to a miogeosynclinal regime, i.e., during the Carboniferous. The patterns of this highly contrastive change in geodynamic setting within a common sedimentation basin and their reflection in the conditions and processes of sedimentogenesis are important and largely unexplored problems. Understanding these patterns would be useful in constructing a more specific definition of the lithologic indicator features of early geosynclinal paleodynamics. It is also essential for describing the evolution of pre-Mesozoic sedimentogenesis in the Northern Verkhofan region on a regional scale. The available data on the paleogeography of the Carboniferous for this region [4, 7, 8] are fragmentary compared to our knowledge of subsequent epochs. Studies in this region could have useful practical application because some of the Middle and Late Paleozoic sediments are metalliferous [2, 5] and it might be possible to define how the mineralization in them was controlled by facies in more concrete terms.

The stratigraphy of these Northern Verkhofan region sediments was developed in the early 1970s primarily by A. S. Kashirtsev. Other investigators included I. M. Biterman, A. A. Mezhevika, L. A. Musalitin, and A. A. Naumov (see [7, 11-13, 23, 25, 36-38]). B. S. Abramov [1] studied the stratigraphy of the Southern Verkhofan region. The subdivision of rock strata into suites and subsuites defined by these authors are still used for regional geologic mapping [32,33]. We adopted them as the basis for our lithologic-facies reconstructions. We are aware that the dating of certain suites remains unresolved, as has been noted by some of the above-cited geologists. The Devonian/Carboniferous and Carboniferous/Permian boundaries remain blurred, depending on which group of faunal remains is used as the basis [12]. There is also uncertainty about the Middle/Upper Carboniferous subdivision [18]. Nevertheless, the local lithostratigraphic units are continuously traceable over tens and hundreds of kilometers in plan, so that by lithologic-facies analysis one can reconstruct the overall sequence of geologic events in space and time with some reliability, regardless of the absolute datings. For this reason, the unresolved stratigraphic problems do not interfere with our reconstructions. Our difficulties are mainly associated with the fact that Carboniferous and Devonian outcrops are concentrated in inaccessible locations.

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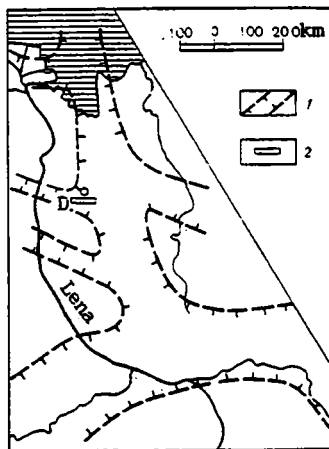


Fig. 1. Distribution of Middle Paleozoic paleorifting zones in the basement of the miogeosynclinal complex (a simplified diagram [5, 9, 16, 17, 47]): 1 — boundaries of paleorifts; 2 — portion of the section on the Soguru-Uel'-Siktyakh River. Circle marks the location of the upper reaches of the Ulakhan-Unguokhtakh River; D = Dzhardzhan LPS.

For a number of years we had the opportunity of studying these rocks in the Kharaulakh and Orulgan ridges. These explorations were especially detailed at the upper reaches of the right tributaries of the Lena: the Dzhardzhan (south) and the Ulakhan-Unguokhtakh (north). In 1991 we performed a detailed exploration of the transection across the course of Carboniferous outcrops in the latitudinal valley of the Soguru-Uel'-Siktyakh River, which is nearest to the Dzhardzhan (see Fig. 1). We earlier explored sediments at the upper reaches of the Ulakhan-Unguokhtakh and even further north in a joint study with Pichugin [45]. The materials collected form the basis for our present report, because they provide new information on Paleozoic sedimentogenesis. Additional data are borrowed from the literature.

AN ESSAY ON THE PREHISTORY OF SEDIMENT FORMATION

A system of grabenlike linear platformal structures (LPSs) existed during the Devonian in the territory of the present Late Paleozoic-Early Mesozoic miogeosynclinal trough in the Verkhoyan region and its immediate surroundings. These structures inherited a system of Late Precambrian rift-type troughs [16, 17, 21, 44]. The structures stretched sublatitudinally (at the lower reaches of the Vilyui River), longitudinally (at the present site of the Orulgan and Sette-Daban ridges), and diagonally (the Dzhardzhan LPS of this section stretched from the Dzhardzhan and Unguokhtakh interfluvium to the northwest, passing over into the Kyutyungdin graben of the Lena-Olenek interfluvium). The strata consist of variegated terrigenous-carbonaceous-evaporitic and volcanogenic-sedimentary rocks covered by basalts. The latest studies of these units by Bulgakova and Kolodeznikov [5] led to the following conclusions.

First, all Devonian LPSs were filled by sediments of mainly shallow seas and lagoons which belonged to a common water body. This conclusion is based on the presence of synchronous transgressive—regressive sedimentation cycles in territorially separated segments.

Second, they arrived at an essentially new thesis that spreading systems arose in the Middle Paleozoic (as opposed to the Late Paleozoic, as commonly believed) and that the migration of spreading structures was consistent in the lateral direction from the eastern margins of the Siberian continent to the west. They remarked: "Since the Kolyma-Alazei spreading system was formed in the Early Devonian, it separated the Alazei block from the Kolyma microcontinent. During the Famennian, the Yana-Indigirka spreading system was founded (or rejuvenated?), which for a long time (Late Paleozoic-Mesozoic) defined the eastern border of the Siberian continent and the position of its continental slope. The series was completed by formation of a Visean deep-sea trough at the site of the Verkhoyan rift system" [5, pp. 191-192].

We discuss the "deep-sea" nature of this trough somewhat later. We now note an additional specific feature of the structure of the sedimentary filling of the Devonian LPS: the absence of any significant submarine-deltaic clastic alluvia. In some locations, one finds sediments with the features of proluvial accumulations by irregular water streams.

The Devonian climate in this region is known to have been arid, and the first clear signs of humidization are dated by the Namurian [8]. This indicates that the land arising on the LPS during the Devonian still lacked developed river systems. Such systems already began to be formed in the Anabar landmass at the Devonian/Carboniferous boundary. An early sign of this process can be observed in the Dzhardzhan LPS, where oblique stratified alluvial textures have been described [5] in the upper section of the Artygan suite, tentatively dated as Upper Devonian-Lower Tournaisian [37]. This suite is underlain by a member of the sulfate rocks of the Atyrkan suite, where an Eifelian coral was found amid dolomitized limestone lenses. In turn, the Artygan suite is covered conformably by the Agakukan terrigenous suite, which contains faunistic remains of the top of the Tournaisian, Viséan, and Serpukhov stages [38]. As we will see below, the first signs of submarine deltaic accumulations become typical for various lithologic varieties in even younger suites (Bulykat, Setachan, and others).

Thus, submarine deltas began to appear in the very beginning of the Carboniferous in the interfluvium of the lower reaches of the modern Dzhardzhan and Ulakhan-Unguokhtakh rivers. They later evolved intensely as an element of Late Paleozoic and Mesozoic formations of the Verkhoyan miogeosynclinal complex [2, 10, 24, 28, 45].

STRUCTURE AND GENESIS OF THE CARBONIFEROUS IN THE DZHARDZHAN/ULAKHAN-UNGUOKHTAKH INTERFLUVIUM

We now describe the results of lithologic-facies analysis performed by us in a description of the sections of the Soguru-Uel'-Siktyakh Valley, which exposes Carboniferous rocks across their course (see Fig. 1). The rocks occur at a low angle and are crumpled to 10-35 km wide box-like folds with a 10-15 to 30-40° slope of layers on wings and a virtually horizontal occurrence in the axial parts of folds. The formation pattern is compounded by systems of longitudinal and diagonal faults and intense cleavage zones.

The exposed lower portion of this section is seen at the core of one of the anticlines uncovered by the middle part of the Soguru-Uel'-Siktyakh River bed and its right tributaries. They are dated by the Setachan suite of the Middle Carboniferous, whose stratotype was described in 1966 by Musalitin and Solomina [23,36] at the intersection of the Nimingde river basin near the Setachan stream 160 km south of our intersection. The following floristic remains were recorded in this location: *Angarodendron obrutschewii* Zal., *A. zalesskyi* Radz., and *Angaropteridium cardiopteroides* (Schmalh) Zal. [38].

Thin bituminous coal interlayers have been described in the same suite 50 km west of our intersection in the Uel'-Siktyakh river basin [7]. Finds of marine fauna (primarily brachiopods, more rarely ammonites) were described with increasing frequency in sections of the formation further to the southeast.

The suite is classified by Ammonoidea as a *Branneroceras-Gastricoceras* zone of the Bashkirian stage. It is underlain conformably by sandstones with coaly siltstone and argillite interlayers of the Bylykat suite and dated by flora as belonging to the Serpukhov stage [38].

A small fragment of the top portion of the Setachan section on the Soguru-Uel'-Siktyakh River is shown in Fig. 2. It is one of the rhythms which multiply recur. Its structure resembles a typical section of a paleodeltaic branch described by Kelling and Jordan in the Carboniferous of southwestern Wales [26, Vol. 1]. Each such rhythm ranges in thickness from a few meters to 15 m and begins with coarse- or large-grained sandstones with a disorderly texture and characteristic differently oriented inclusions of black scree and breccia, argillitic (originally clayey) particles corresponding to the composition of the underlying substrate. These particles exhibit peculiar shapes: angular on one side and rounded on the other. Some were subjected to secondary deformation, which means that there were not lithified matter through sedimentation but were shreds of a pasty sedimentary mass that had not yet solidified. This is a characteristic feature of accumulations of a powerful stream in the side and central parts of an eroded valley within a submarine delta. Up the section, the sandstones are unclearly stratified and show signs of interstratal erosions and deformations of uncompacted sediment. Clear signs of wide oblique unidirectional converging stratification of stream type later appear in them, with a series of layers ranging in thickness from tens of centimeters to a few meters. The stratification gradually becomes randomly directed. At the top of rhythms, these sandstones give way to poorly sorted small- and fine-grained and silty varieties with slightly expressed current ripples and bioturbation traces. These are signs of weakening of stream intensity. They are overlain by

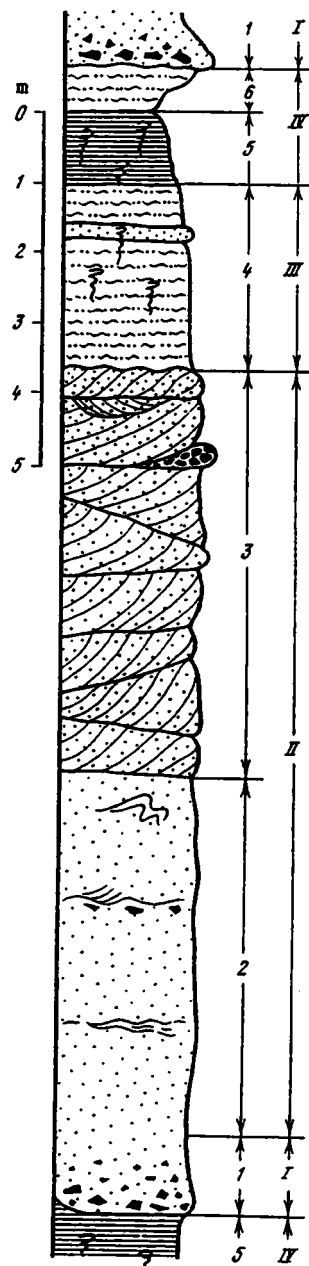


Fig. 2. Section of a rhythm from the Setachan suite (numbers indicate lithotypes (1-6) and their genetic interpretation (I-IV): 1-3 — sandstones from coarse to medium-grained (1 — massive with scree and rubble of underlying rocks, 2 — unclearly stratified with traces of erosion and deformations of uncompacted sediment, 3 — with large oblique stratification, truncated and unidirectional at the bottom, diversely directed at the top, sometimes with gravelite lenses); 4 — fine-grained micaceous silty sandstones with signs of current ripples and bioturbation; 5 — banded-stratified argillites and siltstones saturated with coaly attritus and bioturbation; 6 — silt-sandstones with lumpy separates; I-III — sediments filling the washout channel (I — initial erosional stage, II — main stage where the signs of washout reflect frequent floods and oblique stratification indicates migration of bars, III — period of subsiding activity); IV — sediments of depressions between bars.

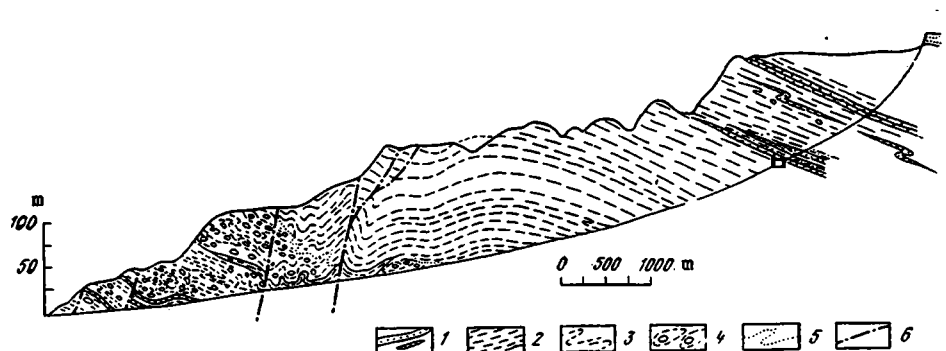


Fig. 3. Fragment of the Sieder suite section on the northern bank of the left branch at the source of the Soguru-Uel'-Siktyakh River: 1 — sandstones beds and lenses; 2 — predominant siltstones and argillites; 3 — ditto, crumpled to slump folds; 4 — mixtites; 5 — facies boundaries; 6 — faults (rectangle indicates the site of Fig. 6).

dark gray to black silty argillites saturated within layers by disseminated organic humous matter: vegetable attritus with low-angle, wavy, fine, continuous or interrupted stratification, imprints of current ripples, and sometimes vortex-like microtextural sediment roiling. The structural-textural features resemble the typomorphic characteristics of flood valley sediments, but are distinguished from them by an absence of distinct remains of roots and abundant traces of bioturbation. These are probably sediments of lagoons or lows between delta accumulations. They are found in close paragenetic association with the above-listed formations of these bodies and alternate with them in multiple order, with recurrence every 10-15 m (see Fig. 2).

Such rhythmicity could have been formed by a sudden shift of channels-branches of the submarine delta that were filled with the coarsest material against the background of general subsidence of the basement floor.

An additional argument in favor of the paleodeltaic origin of these formations is their position in the general facies series of synchronous strata and their relationships to the under- and overlying rock complexes. Littoral alluvial plain sediments with bituminous coal interlayers are predominant to the west of this location (in the Uel'-Siktyakh river basin) as elements of the Setachan and Bylykat suites. Sediments with brachiopods and other marine fauna are found to the southeast (as mentioned above). This intermediate position of this submarine delta is consistent with the general setting, which is also true for the position of the deltaic formations in the vertical facies series. The underlying Devonian-Late Carboniferous rock complex consists of shallow shelf and seafloor terrigenous-carbonate accumulations. The overlying strata of the Yupenchin suite are mainly represented by genetic types of deeper marine environments, reflecting the transgressive direction of the development of the sedimentation basin during this time interval.

These are units with a total thickness of some 600 m which gradually give way up the section to mainly silt-pelitic rocks with rare interlayers of Yupenchin sandstones from 500 to 1000 m thick. These in turn are covered by terrigenous sediments of the Setachan suite more than 850 m thick (illustrated fragmentarily in Fig. 3). The Yupenchin rocks contain numerous remains of brachiopods and goniatites, less often crinoids, pelecypods, gastropods, and foraminifers. These remains date them as the Middle Carboniferous within the top of the Bashkirian, possibly bottom of the Moskovian, stage [23, 26, 38]. The Sieder suite is tentatively dated as the Middle-Upper Carboniferous without further details based on rare finds of brachiopods *Yakutoproductus cheraskovi* Kash., *Brachythyridina kharaulakhensis* (Fred), and others, and at the very bottom goniatites *Stenopronorites karpinskii* Lib., *Yakutoglaphyrites involutum* (Popow), and others. However, Permian foraminifers have been found in the same suite [7].

The build of these suites shows that formationally they belong to the same unit. They were formed by a limited set of genetic types of marine sediments with succession in section and in plan, which according to Frolov's classification (1984) belong to four groups: fluvial (or flow-related), submarine-eluvial, colluvial, and stagnant-calm water. Background sedimentation products are most common in the Yupenchin and western outcrops of the Sieder suite: these are dark gray unclearly stratified argillites separated by finely dispersed sapropel-humus organics. They are often separated by layers of siltstones (0.1 to 1.5-2 cm thick with 5-15 cm intervals). The siltstone layers consist of lenses and are interrupted. Under a microscope one observes in them signs of oblique intermittent microstratification, i.e., traces of a weak dynamic sedimentation environment (Fig. 4). On the other hand, there are signs of frequent pauses in sedimentation, expressed in

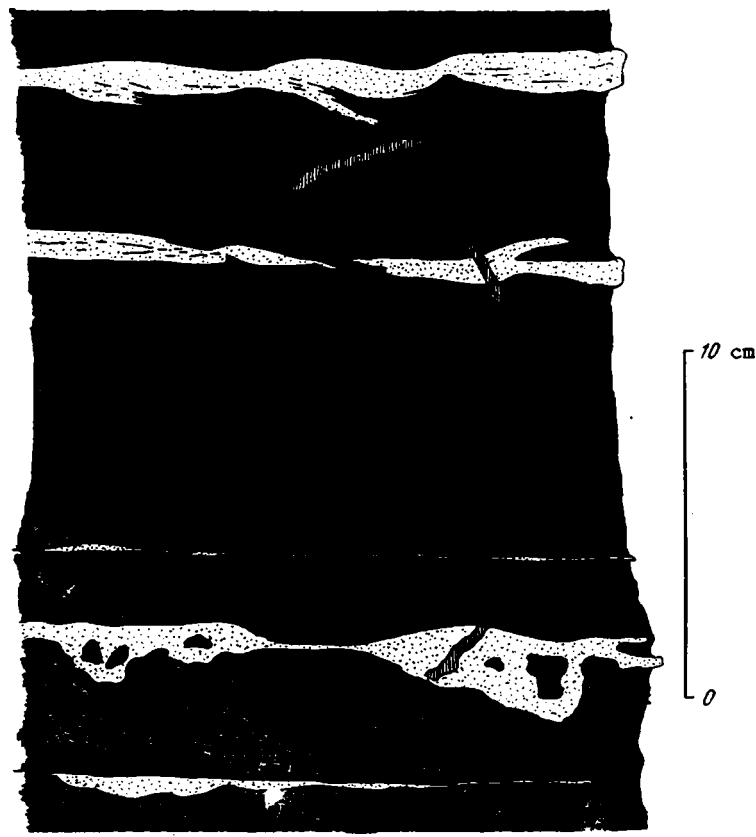


Fig. 4. A detail of the structure of the Yupenchin suite: black background = silt-pelitic rocks; shaded areas = sandstones and coarse-grained siltstones; hatched areas = traces of burrows.

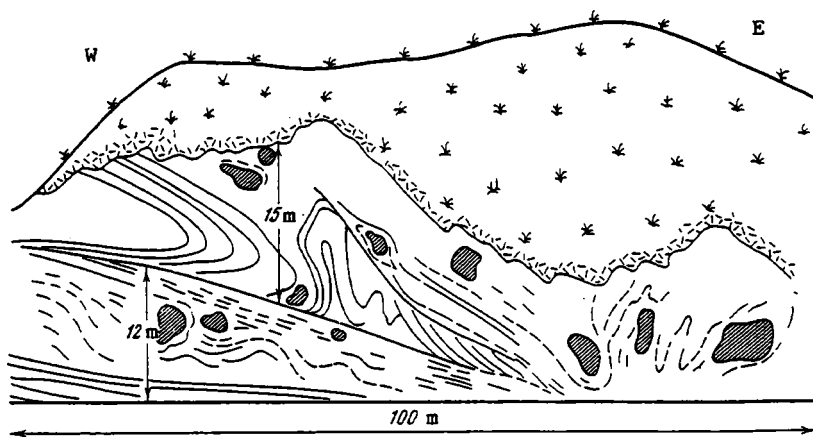


Fig. 5. Submarine slump formations of the Sieder suite at the upper reaches of the Soguru-Uel'-Siktyakh River: solid lines indicate reliable, and dashed lines hypothetical, boundaries of layers in the silt-pelitic rock strata; hatched = sandstone and siltstone blocks (drawing by O. V. Yapaskurt).

uneven forms produced by squeezing silt into a loose oozy substrate and development levels with fine burrows of worms and other traces of bioturbation. More often than others, this type of sediment contains remains of crinoid members in the same position as in life (less often, shifted), fine-walled brachiopod valves, and other marine faunal remains.

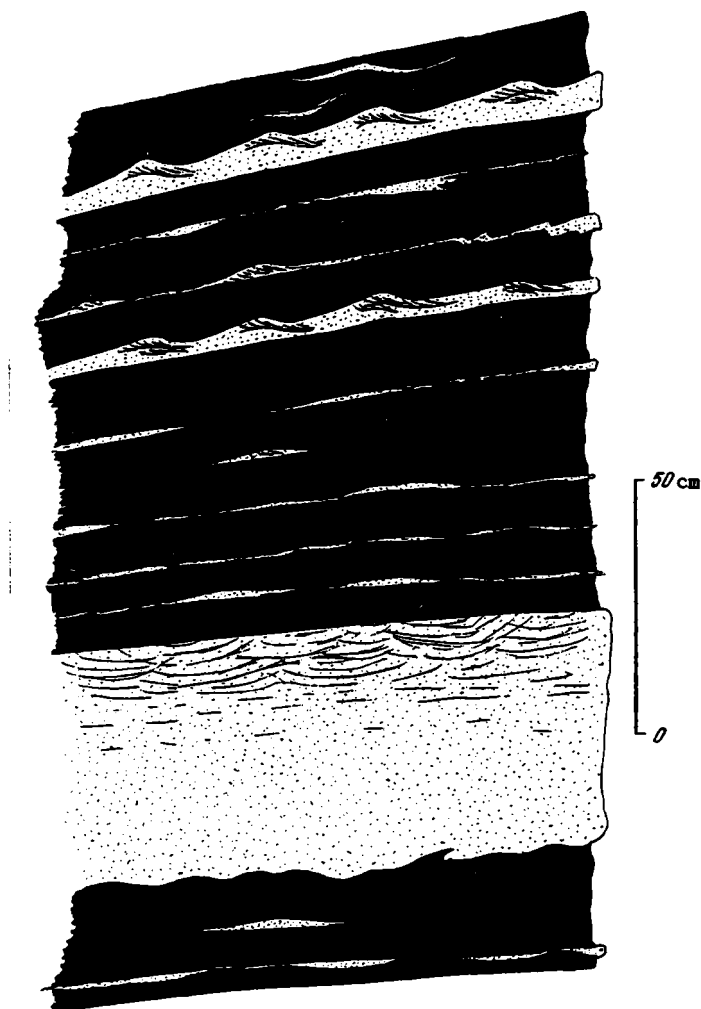


Fig. 6. Detail of the structure of the top portion of the Sieder suite (see Fig. 3). Notations as in Fig. 4.

All these features classify these formations as genetic types of submarine-eluvial and fluvial groups accumulated on interdeltic parts of the shelf. In eastern outcrops of the Sieder suite at their level, one observes common mixtitic submarine-colluvial accumulations (debrites) with slump dislocations of different magnitude (Fig. 5). In plan, they exhibit clear structural-tectonic control: along the zone of the Unguokhtakh deep fault from the northwest to the southeast; from the Kharys stream (right tributary of the Ulakhan-Unguokhtakh) to the upper reaches of the Soguru-Uel'-Siktyakh River.

Other investigators have described gravity slump folds at different stratigraphic levels of the Verkhoyan complex [2, 35]. They also observed control by zones of long-lived faults. Far to the northeast of this area, Andreev [2] noted a common presence of such dislocations in the Permian near the Boguchan fault.

The Unguokhtakh fault apparently played the same role with respect to Carboniferous rocks. We will return to this later. We now examine the morphology of these formations. They are largely similar to "debritic-landslide facies gravitite complexes" as defined by Khvorova [42], the gravitites described in the Jurassic sedimentation basin of the North Caucasus by Gavrilov [6], as well as in differently aged sediments of marine basin depressions observed by lithologists in other parts of the world [26, Vol. 2]. In our case, one observes highly diverse manifestations of gravitational displacements of lithified or semilithified sediment. These are usually fragments of sand or silt beds ranging in shape from lenses and blocks and in size from a few centimeters to 1-1.5 m, sometimes even larger (to 5-10 m and more) (see Fig. 5). They are distributed at random in an enclosing argillite member or in argillitic siltstones and are locally oriented across the course of this member. On the surface, the blocks are enveloped by slightly discernible thin layers of surrounding rock. The sedimentation

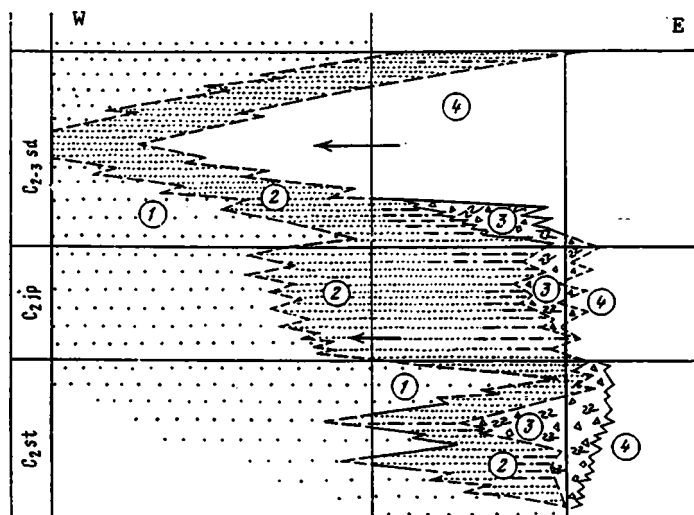


Fig. 7. Evolution of sedimentation settings during the Carboniferous in the interval between the source and the middle reaches of the Soguru-Uel'-Siktyakh River (within vertical lines) and on adjacent territories. Facies complexes: 1 — predominantly sandy sediments of deltaic channels, estuarine bars, and proximal foredelta formations and pelitic sediments of lagoons; 2 — grainy, sandy, and silty stream sediments, fillings of submarine washout pits, formations of the distal part of foredelta cones and intradeltaic shelf sections; 3 — mixtitic submarine-colluvial accumulations near the rim of the floor ledge in a kettle-shaped sea basin; 4 — silt-pelitic C_{org} saturated hemipelagic sediments of depressions combined with seafloor current sediments. Vertical lines delineate extra-scale intervals symbolizing accumulation stages of suites (bottom to top): Setachan, Yupenchin, and Sieder. Arrows indicate direction of transgressions. Facies boundaries which have been traced are marked by solid lines. Hypothetical boundaries are indicated by dashed lines.

stratification inside the blocks is poorly expressed, if at all. Its orientation does not correspond to the arrangement of the strata of the surrounding silt-pelite bed. Some blocks and lenses bear traces of plastic deformation and even a semi-twisted "strudel" texture. Such poorly sorted formations and the surrounding strata can be classified petrographically as mixtites or diamixtites [42]. Genetically they correspond to accumulations of submarine mud/rock streams. Submarine slump folds are found in the same section (see Fig. 3). They too vary in scale: from microscopic disharmonic interstratal folds caused by deformation of S-shaped semicompact sediment to bent strata forming disharmonic folds tens of meters in amplitude. The local development of such folds at sites where strata generally occur at a low angle (see Fig. 3) and their paragenesis with mixtites and separation from over- and underlying members proves their cosedimentary rather than late tectonic origin. On the other hand, the notion of cosedimentary origin is provisional, because, judging by the texture and structure of these formations, landslide processes involved sediments which by then had already passed through partial diagenetic compaction.

The linear arrangement of space localization indicates a deep bend in the paleorelief of the basin floor that existed nearby and was apparently associated with cosedimentary rupture faults.

Sieder suite outcrops also include an additional series of genetic types of marine sediments. Aside from submarine-colluvial formations, this type succeeds the latter facially in the more eastern outcrops of the suite (i.e., at locations farther from the littoral belt). These are mainly black unstratified argillites (in 5-15 cm thick layers) and brownish-gray siltstones separating them, or fine-grained sandstones (ranging in thickness from a fraction of a millimeter to a few centimeters). These rock varieties form members from tens to hundreds of meters thick. The argillites in them are saturated with C_{org} (from 2 to 5.2%) with a predominance of the sapropel component. No microfaunistic inclusions are found. This fact, as well as the uniformity of the composition and the disorderly texture, suggest that these rocks can be classified, with some reservations, as hemipelagic background accumulations. The siltstones and sandstones are probably sediments of bottom streams (along the feet of escarpments) and possibly spasmodic streams from pits (in distal parts of foredeltaic vanes).

The structure of some of the fragments in the sections of these members is similar to the photograph of an exposure published in [26, Vol. 2, p. 158], which is interpreted as a "fine-grained turbidite with fibrous siltstone interlayers: Cambrian–Ordovician Halifax formation in Nova Scotia." At this point we do not postulate this direct analogy, considering possible convergence of textural features. If one compares these units with granulometrically similar interdeltaic areas of the shelf, certain differences can be distinguished. Specifically, bioturbation is less common. Polished sections at small magnifications indicate a peculiarity in the microstructure near the base of the argillite layers. One observes multiply recurring very fine (0.5–2.5 mm) layers consisting of silt grains washed off clay impurities with obvious signs of gradational sorting and traces of erosional boundaries with the underlying pelitic substrate.

The siltstone layers sometimes increase in thickness to a few centimeters, as illustrated by Fig. 6 (top). The siltstones then appear as chains of small lenses convex at bottom and flattened on top, or exhibit a consistent longitudinal arrangement with asymmetric fibrous top surfaces and slight signs of oblique unidirectional convergent lamination. The latter apparently represent traces of current ripples, while the former represent material with ripples eroded by subsequent obviously spasmodic streams. The position of these genotypes in the general facies series is equivalent to flysch, but, to the best of our knowledge, no classical flysch formations are found in this section or any other Carboniferous exposures in the Northern Verkhoyan region. We discuss the possible causes of this later on.

Apparently, the complete set of conditions necessary for development of a flysch formation was absent from this location (aside from steep seafloor ledges, flysch formation requires certain ranges of absolute depth, the existence of large canyons, powerful contour streams, and other geomorphologic and hydrodynamic factors).

Another characteristic group of genetic types illustrated in Fig. 6 (bottom) occurs in close paragenetic unity with these sediments. These are layers of light-gray massive sandstones, usually fine-grained, with sharp contrast at the roof and the base. Their thickness ranges from 0.3 to 1.7 m, and they extend across the course and are measured by hundreds of meters and sometimes a few kilometers. They can be distinguished from other sandy sediments (discussed above) by several specific features. Their clastics are always well sorted and poorly rounded. They are originally piled without admixture of an intergranular matrix (in the course of catagenesis, secondary conformal-regeneration structures later became widespread in these rock varieties). The textures are disorderly within most of the layer; only near the roof are some signs of crosswise lamination observable. Saucer-shaped concave forms are found at the base of layers, which are interpreted as signs of the sand mass squeezing out dents in hydrated oozy soil. These feature resemble those of sediments of grain streams according to the descriptions in [41,42]. However, they are peculiar: no massive tongue-shaped and furrowlike hieroglyphic patterns are seen, as opposed to accumulations formed by high-density streams in the North Caucasus [6] and elsewhere. This can be attributed to the shorter duration of sedimentation pauses in the paleo-Verkhoyan basin, so that the clay substrate was not properly lithified before it was covered by matter from the next stream.

All these formations alternate in a certain sequence from bottom to top in the section and across the course. The diagram in Fig. 7 illustrates transgressive-regressive cycles in the evolution of the paleobasin during the Carboniferous and Early Permian. The transgression maximum falls on the middle of the formation time of the Sieder suite. The regression corresponds to its end and the beginning of accumulation of the next (Lower Permian) Unguokhtakh suite.

A similar picture is observed in more northerly areas in Kharaulakh ridge and the lower reaches of the Lena [45], though submarine-deltaic and submarine-colluvial sediments played a lesser role in those territories.

A MODEL OF THE STRUCTURE OF MARINE BASINS DURING THE POSTRIFTING STAGE OF THE FOUNDATION OF THE VERKHUYAN GEOSYNCLINE

Returning to the genetic features of the Carboniferous, we note that they indicate clearly unstable hydrodynamic environments and pronounced articulation of the seafloor relief. The relief was probably inherited from faults with the configuration of older rift valleys. This is confirmed indirectly by localization of submarine-slump bodies near the suture of the Unguokhtakh fault, which stretches along the northeasterly external boundary of the Dzhardzhan LPS. The direction of the sides of this fault apparently experienced inversion during the Carboniferous, because the deepest of the known facies are situated to the northeast of its fissure plane.

One is hard put to answer the crucial question as to how deep the "gaps" in the seafloor were formed in that area, given the similarity of pelagic sediments in active hydrodynamic settings and in shelf lows. The only clue is offered by analysis of facies series, which for this region suggests the following conclusions.

We have established a convergent cooccurrence of genotypes formed at different depths in some of the levels of the Middle and Upper Carboniferous section, particularly in the upper reaches of the left branch of the Soguru-Uel'-Siktyakh River (based on observations with perfect exposure, where the probability of postsedimentary tectonic contacts is eliminated). The presence of large crinoid fragments oriented across the layering (i.e., buried in situ) in some rocks and traces of wave ripples show the existence of shallow environments (on the order of 50 m, but not more than 200 m). At the same time, large slump folds with debris accumulations (see Fig. 3) are widespread in the upper- and lower-lying rock members. The large size of these units (amplitudes of tens of meters) shows that the slump ledge must have been an elevation several orders of magnitude greater than these amplitudes. This is also indicated by the large size of blocks and separates units, because they could only be moved by energy impossible without a large depth gradient, which would apply a sufficient gravitational force to these rock blocks. A conservative estimate shows that the ledge could not have been less than 500 m, more likely 1-1.5 km in height. This is also confirmed by sediments with clear hemipelagic signs (see above).

The close cooccurrence of the latter with shallow-sea formations suggests a paleotectonic sedimentation mechanism with alternation of long lulls and repeated impulsive tectonic "fallthroughs." The bottom of the resulting gaps was covered by sunk shallow-sea sediments which were covered by neighboring shallow-sea lithified formations sliding from above. These, in turn, were subsequently buried under silt-pelitic hemipelagic ooze and granular and other high-density stream alluvia brought periodically from the slope and distributed by bottom currents. Such a trough would be gradually filled by sediments but would not reach the stage of complete compensation before the next impulse of block sagging at its bottom. This mechanism would create a rhythmic repetition of facies in sections, but it was not its only cause, because eustatic fluctuations of sea level also played a certain role (this issue is outside of the scope of our present investigation; it was described in [46, 47]).

Considering the large thickness of hemipelagic accumulations and their saturation with organic components (diagenesis of these sediments took place in strongly reducing settings [45]) and the traces of bioturbation in them (though less pronounced than in shelf sediments), we conclude that typical pelagic ooze of abyssal sedimentation settings is entirely absent from them.

The paleobasin formed during the Carboniferous was a moderately deep bathyal basin-shaped sea. It had a narrow littoral-shelf platform, indirectly indicated by poor rounding of clastic grains in virtually all lithologic sandy rocks and the paucity of shell detritus. River alluvia brought from the western or southwestern landmass were the main sources of terrigenous material. They accumulated at a rate close to avalanche sedimentation [2], judging by the thickness of the above-mentioned suite (total thickness of 3-4.5 km). The initial catchment area capable of supporting this evolution must have had to be extensive (almost comparable to the size of the paleobasin), because the relief at the Devonian/Carboniferous boundary in the Eastern Siberian Platform was for the most part peneplaned [3, 8, 27]. On the other hand, its articulation consistently intensified during the postrifting period, as indicated by the consistent increasingly polymictic character of clastic matter of sandstones up the section [45]: from mainly quartzose in the Bylykat suite and the bottom of the Setachan suite, to quartzose-graywacke and arkosic-graywacke compositions in the Sieder and Unguokhtakh suites.

Deltaic alluvia also advanced consistently northeast and deep-sea facies advanced in the same direction [2, 10, 24, 45] as a result of the extremely intense rate of expansion of the sedimentation basin during the miogeosynclinal tectonic regime. This rate was faster than the sedimentation rate in the initial stage of this regime, as indicated by the predominant amount of silt-pelitic varieties in the Carboniferous sediments. The frequent lulls in sedimentation and landslides also suggest insufficient compensation of troughs by sediments, i.e., subsidence was faster than sediment accumulation. This in turn means that marine sedimentation in the geodynamic settings of the spreading predominant during the Carboniferous took place under a certain deficit of clastic matter, despite the fact that it was supplied by an avalanche mechanism from the river system that had taken shape in the meantime. This may also be a reason for the absence of flysch strata in this (initial) formation stage of this basin.

* * *

Multiphase rifting responsible for destructive alteration of the continental crust of the North Asian craton during the Riphean and Early and Middle Paleozoic largely predetermined sedimentation features of the Late Paleozoic and Mesozoic during the evolution of the Verkhoynan miogeosyncline. Massive activation of spreading systems initiated in the Devonian resulted in block sagging of the sedimentation basin basement, which inherited its configuration from older rift structures. Lithologic-facies and stadial-petrographic data indicate that impulsive sagging intensified and spread to wider

territories during the Carboniferous. This is consistent with Milanovskii's theory that extension of the earth's crust responsible for these saggings [15, 22] evolved during the early development stages of a geosyncline in a pattern essentially different from that of rifting epochs [21, 22]. This early geosynclinal process was so intensive that depressions were not fully compensated by sediments. On the other hand, in our case, no abyssal basin was formed. Though sedimentation took place during the Carboniferous under a certain scarcity of clastic material, the sea that filled the troughs was relatively shallow (bathyal). It was a basin-type sea with a poorly developed littoral zone, where terrigenous matter was massively supplied by river systems but not through internal "cordilleras." It has certain common traits with paleogeographic reconstructions made by Khvorova and Il'inskaya [42] for the Late Devonian paleobasin in the South Urals.

These parameters are different from those of oceanic margins as defined currently. This confirms a basic difference between the tectonic structures of geosynclinal basins and the world ocean [43]. Our results also support the concept of a formational peculiarity of the Late Paleozoic in folded belts [19, 20, 31, 40], indicating that the present clear differentiation of features between intracontinental and marginal continental sea basins did not yet exist at the time.

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LITHOLOGY AND CONDITIONS OF ACCUMULATION OF LOWER CAMBRIAN DEPOSITS IN THE LOWER REACHES OF THE BAYAN-KOL RIVER (CENTRAL TUVA)

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A description of the facies character and distinctive features of the mineral–petrographic and petrochemical composition of Lower Cambrian deposits in the lower reaches of the Bayan-Kol River is given. It is shown that the terrigene, volcano–terrigenous, and carbonate sediments that have developed here characterize a sea basin with dissected topography of the sea bed, intensive subaerial and subaqueous volcanism, and numerous archaeocyathian-algal reefs. The accumulation of clastogene sediments occurred as a result of the erosion of the Tuva Mongolian mass and local volcanic edifices. Analysis of published data attest to the existence at this time of analogous conditions within all of Western and Central Tuva.

The Lower Cambrian deposits of Central Tuva are represented by volcanogenic, volcano–sedimentary, and sedimentary formations, including basalt, spilite, andesite, tuff, and tuff breccia, detritus (principally rudaceous varieties), limestone with archaeocyathae, algae and trilobites, and chert and clay chert. This complex is characterized by nonpersistence of structure and rapid lateral transformation. The rocks are multiply dislocated, worked into folded systems, and divided into blocks by means of numerous dislocations with breaks in continuity, moreover, these dislocations have experienced significant horizontal and vertical displacements.

Studies carried out by N. N. Kheraskov [14], N. A. Berzin [1], and A. B. Dergunov [4] have demonstrated that in the early Cambrian the territory now referred to as Central and Western was situated within an island arc system bounded to the northwest by a large sea basin with ocean-type crust and to the southeast by Tuva Mongolian mass with continent-type crust formed into a reef. This system was characterized by a homodromous series of volcanites, intensive horizontal movement leading to crowding phenomena, the displacement of tectonic plates, and the formation of a differentiated topography.

Tommotian, Atdabanian, and Bottomian stages of the Lower Cambrian, and, possibly, the presence of part of the Upper Vendian have been established in Lower Cambrian deposits. A section of the lower reaches of the Bayan-Kol River belongs to the class of stratified and lithological types of Lower Cambrian deposits (Fig. 1). It was first described as the Bayan-Kol suite [8]; subsequent research led to a subdivision of the suite into the lower Bayan-Kol subsuite and the upper Bayan-Kol subsuite [2]. A. B. Gintsinger et al. [3] suggested retaining the designation, "Bayan-Kol suite," only for the lower portion of the section (lower Bayan-Kol subsuite), and that the upper portion should be considered part of the Uzunsair suite, which had been previously identified by N. S. Zaitsev [6] to the west of the interfluvium of the Bayan-Kol and Ezhim Rivers. It is precisely this scheme which has been followed in the present article.

The total thickness of the Lower Cambrian deposits in the region amounts to 2000–2500 m. Their relation to the subjacent and superjacent formations is not clear. The thickness of each of the suites reaches 1200–1500 m. Opinions as to the time of accumulation of the deposits differ. D. V. Osadchaya et al. [11] correlated these deposits to the upper part of the Atdaban stage and the lower part of the Bottom stage (Sanashtyngol horizon), while A. B. Gintsinger et al. [3] correlated them solely with the Atdaban stage, including the Natalin, Kiisk, and Kameshkov horizons.

In the lower reaches of the Bayan-Kol River these deposits form two synclines (a northern syncline and a southern syncline), separated by an antiform. The structures have sublatitudinal strike, and are complicated by smaller folds and a series of dislocations with breaks in continuity. The axial portions of the synclines are filled with deposits from the

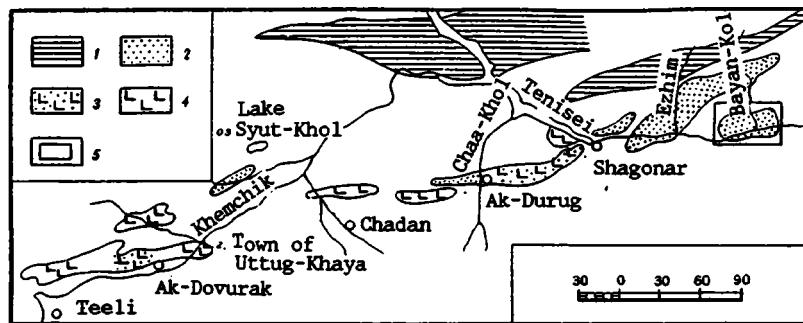


Fig. 1. Regions of localization of Lower Cambrian deposits in Central and Western Tuva. Chingin suite: (1) basaltoid, hyaloclastite, chert, jasperoid; Akduruk and Altynbulak suites: (2) predominantly terrigene deposits; (3) terrigene deposits, basalt, andesite, tuff, hyaloclastite; (4) predominantly basic and intermediate volcanite, hyaloclastite, and tuff; (5) region of detailed description.

Uzunsair suite, while deposits from the Bayan-Kol suite may be found on the surface in the antisyncline and along the northern flange of the southern syncline.

LITHOLOGICAL AND FACIES CHARACTERIZATION

The Early Cambrian deposits of the lower reaches of the Bayan-Kol River are represented by lithologically and environmentally distinct complexes.

The Bayan-Kol suite is composed mainly of detritus (conglomerate, sandstone, gritstone), including individual horizons of tuff and limestone. The thickest (up to 400 m) horizon of the latter elements lies in the lower part of the suite.* Individual lenticular intercalations of limestone with thickness from a few meters up to 40 m are present in its central and upper parts, particularly right at the boundary with the superjacent suite.

The study of the Lower Cambrian deposits of the suite by means of the method of lithological facies developed by P. P. Timofeev [13] demonstrated that these deposits comprise several facies corresponding to the macrofacies of a coastal shoal, such as the pebble sediments of highly labile sea shoals, sandy gravel sediments of labile sea shoals, sandy gravel sediments of periodically drained, labile sea shoals, and silty-sandy sediments of isolated bays and lagoons. Each of these facies is characterized by its own distinctive set of genetic markers.

The facies of pebble sediments of highly labile sea shoals is represented by fine-, medium- and coarse-grained pebble conglomerates, the pebbles being rounded-angular or semirounded, more rarely, highly rounded in shape. The rocks are nonlamimated, slightly graded, often containing inclusions of fine and medium-size boulders, with a significant admixture of sandy gravel material playing the role of a bonding mass. Interacalations and lens which extend beyond the site have formed in the section. The thickness ranges from 1.5 to 10 m.

The facies of sandy gravel sediments of labile sea shoals includes fine-, medium-, and coarse-grained gritstone and medium- and coarse-grained limestone light and greenish gray in color, comparatively highly graded and often containing inclusions of fine pebbles. In most cases the rocks are nonlaminated, though sometimes distinct coarse and fine cross lamination, cross wavelike lamination, or fine cross striated or horizontal lamination may be established as a result of variations in the dimensions of the sandy gravel material or in the layerlike accumulation of silty-clayey particles. The thickness of the deposits varies from a few meters to several dozen meters.

The facies of sandy gravel sediments of periodically drained labile sea shoals resembles in many ways the facies just described and includes fine-, medium-, and coarse-grained gritstone and medium- and coarse-grained sandstone, either nonlaminated or possessing weakly expressed types of lamination analogous to the preceding facies. An important feature of the sediments is that the rocks found there are rose or cherry-red in color and that many of the detritus granules are highly eroded. Thickness varies from 3 to 15 m.

*Some investigators place this horizon in the upper part of the suite [3], though this conclusion has not been adequately proved.

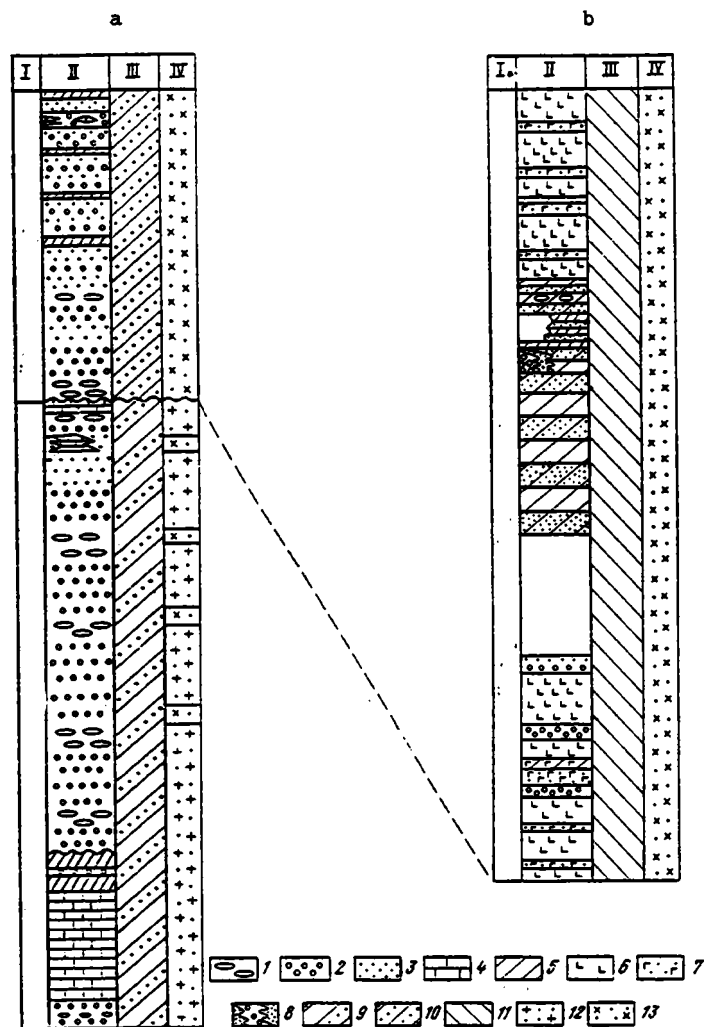


Fig. 2. Lithological column of Lower Cambrian deposits in the lower reaches of the Bayan-Kol River. I: suites; II: lithology; III: conditions of accumulation; IV: terrigenous-mineral associations. (1) conglomerate; (2) gritstone; (3) sandstone; (4) limestone; (5) siltstone; (6) basic and intermediate effusive rock; (7) tuff; (8) blocks of displaced rock; (9) - (11) conditions of accumulation: (9) shallow-water portion of shelf (sedimentary facies: pebble sediment - highly labile; sandy gravel sediment - labile and periodically drained labile shoals; silty-sand sediment - isolated bays and lagoons; carbonate sediment - algal-archaeocyathean reefs; carbonate sediment - calcarenite limestone); (10) shallow-water part of shelf (sedimentary facies: ash sediment - land eruption, rubble-pebble and sandy gravel sediment - perivolcanic gravity flows; carbonate sediment - algal-archaeocyathean reefs); (11) deep-sea part of shelf (sedimentary facies: ash sediment from land eruptions; hyaloclastic sediment - without substantial displacement of material; hyaloclastic sediment - with significant displacement of material; sandy gravel sediment - subaqueous streams; finely interbanded silt, sandy, and carbonate sediment - relatively deep sea; silty-sand sediment - distal part of gravity flows); (12) and (13) terrigenous-mineral associations: (12) quartz feldspar and feldspar-quartz greywacke; (13) volcanomictic greywacke.

The facies of silty-sand sediments of isolated bays and lagoons is composed of coarse-grained siltstone, fine-grained poorly graded sandstone, often with an admixture of gravel and fine-grained pebble material, dark gray in color, frequently with a distinct brownish gray shading, either nonlaminated or possessing a weakly expressed horizontal wavy lamination and turbid textures. The thickness of the sediments varies from a few meters to several dozen meters.

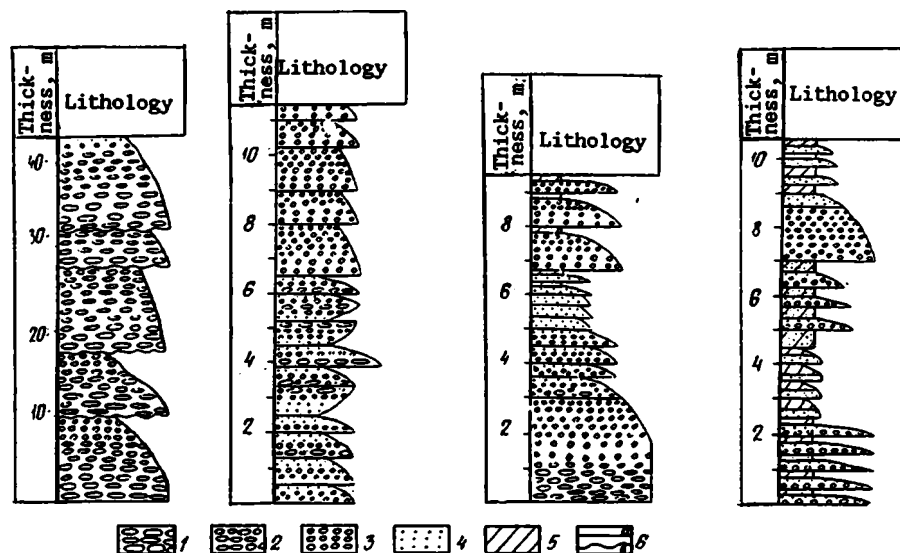


Fig. 3. Types of rhythms in deposits of perivolcanic gravity flows. (1)-(2) conglomerates (1 - rubble; 2 - fine- and coarse-grained pebble); (3)-(5) mixtites with preponderance of material (3 - gravel; 4 - sandy; 5 - silty-clayey); (6) boundaries (a - distinct; b - eroded).

The facies of algal-archaeocyathean reef-created carbonate sediments is represented by an alternation of algal-archaeocyathean bioherms and intercalations of limestone with lumpy jointing or horizontal and wavy lamination. The intercalations are enriched with silty-clayey and sandy gravel material, often containing individual pebbles or pebble accumulations. Independent intercalations of terrigenous rocks are present. The deposits are light gray, gray, or rose in color and form lenticular bodies measuring from a few meters to several dozen meters in thickness. The formation of the facies occurred in a zone in which the behavior of the aqueous medium was highly dynamic.

The facies of calcarenite sediment consists of redeposited carbonate material, including, to varying degrees, crushed fragments of archaeocyathae and algae, with an extremely limited quantity of large remains of these organisms. The rocks are light gray in color, and possess a thin horizontal and wavy lamination. The thickness of the sediment varies from a few meters to 12 m. In terms of conditions of accumulation, they would appear to correspond to several events of subsidence of the sea floor within a shoaly zone that had formerly been characterized by a comparatively quiescent hydrodynamical setting.

In the Bayan-Kol suite (Fig. 2a) the most important features are the conglomerates and sandy gravel rocks from the different facies of highly labile, labile, and periodically drained labile sea shoals. A band of sandy silt sediments from different facies of isolated bays and lagoons around 90 m in thickness occurs in the lower part of the suite directly above the thickest body of limestone.

Among the varieties of limestone the most widely dispersed is the reef facies. The reef facies forms a thick body confined to the lower part of the section, as well as a number of lens of significantly lesser thickness in the upper part of the section. Lenticular horizons of calcarenite limestone have been established near the upper boundary of the Bayan-Kol suite.

The Uzunsair suite of the northern and southern synclines differ substantially both in terms of the set of lithological rock types and in terms of the facies nature of the rock. Within the southern syncline of the suite mainly terrigenous sediment are formed, including conglomerate, greenish-gray mixtite, poorly graded gritstone, sandstone, and siltstone. The latter include individual lens of light gray algal-archaeocyathean limestone and thin intercalations of lithic tuff. The terrigenous sediment belongs to the facies of perivolcanic gravity (spontaneous) flows. They reveal a distinct rhythmic structure, and direct and inverse scaled grading. The forms of gritstone and sandstone which are found are nonlaminated, and besides nonlaminated siltstone there are also present varieties with weakly expressed horizontal and wavy lamination.

The dimensions of the material which form these deposits varies as a function of position in the section of the suite and on the position within each rhythm (Fig. 3).

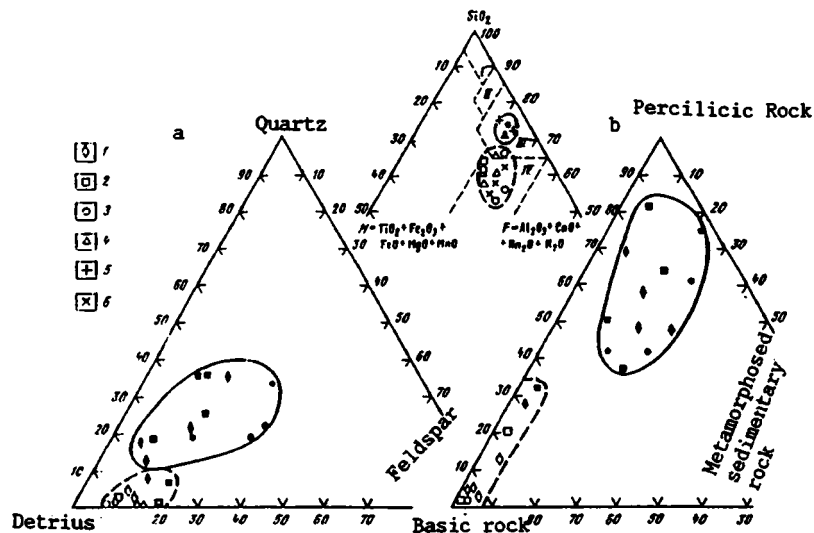


Fig. 4. Relative proportions of rock-forming components and oxides in rocks in the series. Quartz-feldspar of detritus (a) and effusive percilicic rock (basic and intermediate effusive rock) and metamorphosed and sedimentary rock (b); relative proportion of oxides: $\text{SiO}_2 + \text{M}(\text{MgO} + \text{Fe}_2\text{O}_3 + \text{FeO} + \text{MnO} + \text{TiO}_2) - \text{F}(\text{Al}_2\text{O}_3 + \text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O})$ (c); fields of constituents (for each of seven represent elements): I – quartz; II – oligomictic; III – polymictic; IV – volcanomictic; rock types: (1) sandy gravel mixtites; (2) fine- and medium-gravel gritstone; (3) medium- and coarse-grained sandstone; (4) siltstone (filled symbol, Bayan-Kol suite; hollow symbol, Uzunsair suite); (5) granite; (6) basic and intermediate effusive rock [14].

The rhythms of the basal levels of the suite are characterized by a preponderance of rubble and pebble material consisting of sandy gravel material in the bedding of each rhythm and of sandy gravel material with inclusions of rare boulders in the upper parts of the rhythms. The thickness of the rhythms is usually 7-12 m. In the central part of the suite the rhythm bedding is composed of gravely material with a substantial admixture of silty-clayey material, and the thickness of the rhythms at most a few meters. In the upper part of the suite the rhythm bedding forms medium- and coarse-grained sandstone with admixtures of gravel granules and rare small-size pebbles, while the upper parts consist of ungraded sandstone with a large admixture of silty-clayey particles. The thickness of the rhythms varies from a few dozen centimeters to 1.5-2 m.

In the central and upper parts of the suite lenticular bodies up to 25-30 m in thickness composed of several thick rhythms with a preponderance of coarse gravel-pebble material replaced throughout the strike by a series of thin rhythms composed of sandy-gravel and silty-sandy material are often established. These bodies constitute ancient buried river beds (channels) along which the basic mass of matter of the gravity flows traveled.

The rare horizons of lithic and vitroclastic tuff are distinguished from the detritus by a light greenish gray coloring pitted by the surface of a sliding fracture. They are characteristic of the upper horizons of the suite and are confined to the upper silty-sand parts of the rhythms (thickness from a few centimeters to 15 cm). The ash material in these horizons is fully recrystallized, and the structure typical of ash rocks is manifested very weakly.

Lenticular bodies of limestone several meters thick have been established in the upper part of the suite, and correspond to the facies of algal-archaeocyathian reef-created formations.

The formation of deposits of the type of gravity flows is usually ascribed to processes that occur on a continental slope and the foot of the slope. Data have recently been found that attest to the possibility that these types of sediments could have formed within the shelf. Thus, in volcanic regions directly adjacent to land volcanoes and the sea shore such deposits occur in very shallow-water parts of the shelf adjacent to bays and lagoons [9]. Here subaqueous gravity flows represent a continuation of rubble flows (lahar) generated on the subaerial flanks of volcanoes. In view of the fact that the Uzunsair suite occurs right in the shallow-water coastal sea deposits of the Bayan-Kol suite and consists mainly of redepos-

ited volcanic material and contains intercalations of calcareous tuff and lens with archaeocyathan fauna representing shallow-water sediments, it is reasonable to assume that the suite represents just this type of sediment.

In the Uzunsair suite of the *northern* syncline basic and intermediate effusive rock and tuff of these types of rock predominate, along with a restricted development of volcanic breccia, gritstone, sandstone, siltstone, claystone, and rare intercalations of limestone. A diverse complex of facies has been established in the suite: (a) hyaloclastic sediment, material from which has not undergone any substantial displacement; (b) hyaloclastic sediment, material from which has undergone substantial displacement; (c) sandy gravel sediment, consisting of granular flows; (d) finely interbanded silty-sand deposits, from relatively deep sea; (e) clayey sand and carbonate deposits, from relatively deep sea; (f) silty-sand deposits, from the distal part of turbid flows; (g) subaquatorial ash sediment from land eruptions.

The facies of hyaloclastic deposits, material in which did not undergo substantial displacement, embraces volcanic breccia, and volcanite gritstone and sandstone, is grayish-green in color, nonlaminated and ungraded, with significant variations in the dimensions of the material composing the facies. They are formed from the rounded angular and angular detritus of volcanic glass, basic and intermediate effusive rock, and feldspar. The remains of fauna have not been discovered. These sediments form layers several meters thick which are confined to horizons of basic and intermediate effusive rock.

The facies of hyaloclastic deposits, material in which underwent substantial displacement, is represented by volcanic breccia, volcanic gritstone, sandstone, and siltstone, is grayish-green in color, weakly graded, nonlaminated, sometimes with weakly expressed horizontal and wavy lamination. The shape of the fragments forming the rock is rounded angular and semirounded. Remains of fauna have not been discovered. The deposits form intercalations and lens (up to 10-15 m thick) which occur amidst the horizons of basic and intermediate effusive rock.

The facies of sandy gravel sediment of granular flows consists of fine-grained gritstone, medium- and coarse-grained sandstone, grayish green in color, rather well graded, and nonlaminated. The detritus are rounded angular or semirounded in shape. Basic and intermediate effusive rock predominate among them, and quartz, feldspar, and marmorized limestone are present in small quantities. The intercalations are not more than a few meters thick.

The facies of finely interbanded silty-sand sediment from relatively deep sea embraces deposits fine- and coarse-grained siltstone and fine-grained sandstone forming a fine alternation with thickness of the intercalations of from a few millimeters up to 1.5-2 cm. The rock is greenish gray in color, forms a distinct thin horizontal lamination due to alternation of the varieties mentioned above with clearcut boundaries between the individual layers. Remains of fauna have not been discovered. Inclusions of highly rounded effusive pebble and limestone, as well as lumps measuring up to 3-4 m in diameter, formed by alternating intercalations of conglomerate, gritstone, sandstone, and siltstone are present. The facies sediment forms intercalations and bands from a few meters to several dozen meters thick.

The facies of clayey silt and carbonate sediments from deep sea is represented by claystone and fine-grained dark gray siltstone and light gray limestone. The rock often forms a thin (not more than 1 cm thick) alternation of intercalations with horizontal and wavy lamination. No fauna have been discovered in the siltstone or claystone, though accumulations of sponge spiculae are often present in the limestone. In the section these sediments are represented by a band around 30 m thick.

The facies of silty-sand sediment from the distal part of the gravity flows is formed from a thin or fine alternation of dark gray coarse- and fine-grained siltstone and gray fine-grained sandstone with distinct direct and inverse scaled grading and thickness of the rhythms of up to 3-5 cm. The rocks contain inclusions of isolated rounded effusive pebbles and limestone. No remains of fauna have been discovered. The deposit forms horizons and bands several dozen meters thick.

The facies of subaqueous ash sediment from land eruptions embraces vitroclastic and lithic tuff greenish and light gray in color with relics or well preserved ash structure. The dimensions of the ash particles reaches 0.05-0.1 mm. The rocks reveal different degrees of silicification, weakly expressed or distinct horizontal lamination, manifested as a result of different degrees of enrichment with quartz and feldspar grains, and variations in the dimensions of the ash particles. No fauna has been discovered; the thickness of the intercalations reaches several dozen centimeters, sometimes 2 m.

MATERIAL COMPOSITION OF SEDIMENTS

The material composition of the terrigene deposits is heterogeneous and subject to substantial variations. Conglomerates are distinguished by a predominance of basic and intermediate effusive rock (basalt, andesite, diabase, diorite)

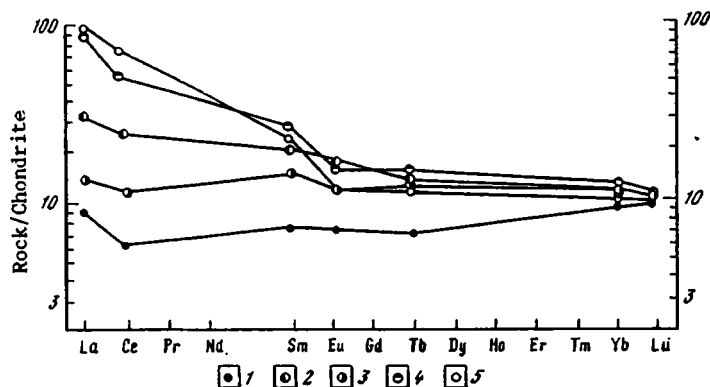


Fig. 5. Distribution of rare earth elements in rocks from the Early Cambrian. (1) basalt; (2) andesite; (3)-(4) medium-grained sandstone (3 – volcanomictic greywacke, 4 – feldspar-quartz and quartz-feldspar greywacke); (5) averaged data for the upper continental crust [12].

which form 65-75% of the pebbles in the Bayan-Kol suite and 90-95% in the Uzunsair suite. Limestone, granite, effusive perclitic rock, rose or reddish chert, clay chert, microquartz, and quartz-mica schist play a sharply reduced role. In the Bayan-Kol suite many of the pebbles have undergone significant weathering, the effusive and granitoid rocks are brownish-red and rose in color due to the presence of iron hydroxide; segregations of iron hydroxides often develop in cracks and interstices. The basic and intermediate effusive rock in the pebbles found in the Uzunsair suite are distinguished by a brilliance of color, whereas the effusive and granitoid perclitic rock is highly weathered.

In terms of the relative proportion of rock-forming components, the sandy gravel rocks vary from quartz-feldspar to feldspar-quartz greywacke (Fig. 4).

Quartz-feldspar and feldspar-quartz greywacke contain quartz at a rate of 18-35%, feldspar 12-35%, and rock fragments 35-65% (Fig. 4a). The quartz is characterized by a preponderance of igneous varieties (isometric grains with inclusions of gas or liquid bubbles, and ore dust). Elongated grains of highly cataclastic quartz from metamorphosed rock and well rounded grains from sedimentary rock are present in lesser quantities.

Plagioclase is represented by albite and perclitic oligoclase; orthoclase is present in the form of isolated grains. These minerals all exhibit significant weathering and contain segregations of brownish clay minerals.

Effusive perclitic rock (dacite, quartz-porphyrite, porphyry-felsite), basic and intermediate effusive rock (basalt, andesite), siliceous rock (silicon, clay chert, and ferruginous clay chert), limestone, microquartz, and quartz-sericitic schist have been established in the detritus present in the sandstone and gritstone. In a triangular diagram, the vertices of which correspond to 100% of the perclitic magmatic rock, basic and intermediate effusive rock, and metamorphosed and sedimentary rock, a broad area with content of perclitic rock from 40 to 85% corresponds to this association (Fig. 4b).

Volcanomictic greywacke in sandy gravel fractions consist of detritus (75-95%), quartz (1-17%), and feldspar (1-18%) (cf. Fig. 4a). The basic and intermediate effusive rock which predominate in the detritus have been significantly altered by weathering processes, and the basic mass in these rocks are highly chloritized and the plagioclase are saussuritized; the grains are semirounded or rounded angular in shape. The fragments of the other types of rocks present in the sandstone and gritstone are analogous to the corresponding types of rock in the association described above, and include, among others, granitoids, effusive perclitic rock, siliceous rock, and others, though in the form of isolated grains. Undetermined residues of microphytolites and sponge spiculae are encountered in limestone grains taken from the sandstone and gritstone of the Uzunsair suite found within the northern syncline.

Feldspar found as a constituent of the association is represented mainly by oligoclase and andesite (up to 35%), and perclitic oligoclase and albite are rarely encountered, often in an intergrowth with quartz. All the feldspar found here are markedly weathered and slightly rounded in shape, though highly rounded feldspar is also present.

TABLE 1. Content of Rare Earth Elements in Lower Cambrian Sediment

Rock	Content, 10 ⁻⁴ %								La/Ib
	La	Ce	Sm	Eu	Tb	Ib	Lu	Σ	
Andesite*	10	20	3,8	1,2	0,66	2,5	0,36	38,52	4
Basalt*	2,6	5,0	1,4	0,49	0,33	1,9	0,33	12,05	1,4
Medium-grained sandstone (quartz-feldspar and feldspar-quartz greywacke)	32	48	5,4	1,1	0,71	2,3	-0,36	89,87	13,9
Medium-grained sandstone (volcanomictic greywacke)	4,6	9,8	3,0	0,89	0,56	2,5	0,38	21,73	1,84

*From the collection of Yu. V. Karyakin.

The description which we have presented shows that, in terms of the collection of rock-forming components, the two associations are similar to some degree. They contain an analogous collection of minerals, though the relative proportions of these minerals are markedly different. In the triangular diagrams (cf. Fig. 4a, b) they form two convergent fields. According to the data of chemical analysis, rock from the first association contains SiO₂ at a percentage of around 72-76%, while rock in the second association, at a percentage of around 52-68%. In a rock classification diagram constructed on the basis of a chemical analysis [7] with vertices of the triangle corresponding to 100% content of SiO₂, and total quantity of MgO, Fe₂O₃, FeO, MnO, and TiO₂, and total quantity of Al₂O₃, CaO, Na₂O, and K₂O(F), both associations are situated in adjacent segments of the fields, which correspond to polymictic (arkose) and volcanomictic varieties. Interestingly, the first association is, in terms of composition, very similar to granite, and the second, to andesite and basalt.

The two terrigene-mineral associations differ substantially in terms of the content and relative proportion of rare earth elements. By comparison with the second association, sandy gravel rock in the first association is characterized by an elevated total content of the elements of this group and an elevated degree of enrichment of these elements with a light fraction. The data presented in the accompanying table show that the content of the seven representative elements in the sandstone of the first association is roughly 4 times greater than in the second association, and, in terms of the La/Ib ratio, differ by almost a factor of 7. It is clear from Fig. 5 that the distribution curve of rare earth elements in the sandstone from the first association is close to the distribution curve characteristic of the upper continental crust as a whole [12], and that distribution curve of these elements in sandstone in the second association occupies an intermediate position between the basalt and andesite curves. These features of the distribution of rare earth elements in the rocks of the two associations reflect a peculiarity of the material composition of the rock: a marked preponderance in the first association of erosion products of granitoids and metamorphosed perclitic rock, and of erosion products of andesite and basalt in the second.

Quartz-feldspar and feldspar-quartz greywacke are characteristic only of the Bayan-Kol suite (cf. Fig. 1), forming the greater portion of its section. Volcanomictic greywacke is present both in the Uzunsair and the Bayan-Kol suite. The former suite includes precisely all the horizons of sandy gravel rock, while the latter is composed of comparatively rare horizons of sandy gravel rock with thickness from a few meters to 10-15 m.

CONDITIONS OF ACCUMULATION

The lithological-facies and mineralogical-petrographic study of Lower Cambrian deposits has demonstrated that these deposits exemplify different conditions of sedimentation, including zones of sea shoals and a relatively deep-water part of the sea. The Bayan-Kol and Uzunsair suites of the southern syncline correspond to the conditions of sea shoals, though each of the suites is distinguished by its own set of facies types of sedimentation.

The deposits of the Bayan-Kol suite were built up in a zone of coastal sea shoals characterized by an intensively dynamic aqueous medium. The conglomerates, gritstone, and sandstone which form the greater part of the suite correspond to precisely these conditions. Periodic drainage occurred in the shallowest waters of this zone, and the sediment itself

underwent intensive weathering, acquiring a dark and cherry-red hue. Poorly graded silty-sand sediments formed in the comparatively rare bays and lagoons.

The setting created by the highly dynamic behavior characteristic of the aqueous medium of coastal shoals produced favorable conditions for the development of calcareous alga and the latter resulted in the formation of large and small reef edifices. This result was also favored by the presence in the region of a very warm climate [5], which made it possible for the water to remain sufficiently warm. Numerous archaeocyathae inhabited the region along with the algae. It is most likely that the bodies of reef-created limestone which remain in the contemporary section constitute only a fraction of the edifices which once existed and which had soon become eroded. One piece of evidence for this supposition is the presence of a rather large quantity of boulders and pebbles, as well as the sand-gravel limestone grains which are found in the conglomerates, sandstone, and gritstone; the erosion and redeposition of material from these edifices was also associated with the formation of intercalations and lens of calcarenite limestone established in the section.

The distinctive features of the material composition of the greater part of the sandy gravel rock, in particular the high content in this rock of quartz, perclitic feldspar, effusive perclitic rock, granite, microquartzite, and mica chert, shows that these rocks accumulated as a result of the erosion of blocks from a continental-type crust. Erosion was confined to regions to the south of the Tuva Mongolian mass, where these types of rock are widely represented in a Vendian complex [4]. Erosion of basic and intermediate effusive rock which predominate in the conglomerate pebbles and in the rock-forming fraction of volcanomictic sandstone or gritstone, rare horizons of which are present in the suite, also played a decisive role. It is entirely likely that the effusive rocks had been small islands which rose up above the surface of the water.

The sediments of the Uzunsair suite of the southern syncline correspond to the conditions seen in sea shoals bordering volcanic islands which had violently emerged above the surface of the water. Large masses of poorly graded material which had accumulated in the sea in the form of sediments of subaqueous spontaneous flows would appear to have migrated down the slopes of the volcano as rubble flows. Lens of biohermic limestone containing the remains of algae and archaeocyathae which are encountered in the clastogene sediments confirm that sedimentation conditions existed in the shallow waters. The presence in the pebble and boulder conglomerates of limestone is associated with erosion of some of these reefs, though the possibility that some of them might have appeared as a consequence of the erosion of analogous forms of limestone found in the Bayan-Kol suite is not excluded. Intercalations of tuff point to manifestations of the explosive activity of the volcano. The gradual slackening off of volcanic activity, a reduction in the height of the volcano, and a smoothening out of its slopes together reflect an upwards thinning out of material throughout the section, a process which is typical of the suite.

The high content in the rocks from the Uzunsair suite of fragments of basic and intermediate effusive rock is in agreement with conclusions drawn concerning the entry of volcanic terrigenous material from the slopes of the volcano. In addition, the presence of a small admixture of quartz, effusive perclitic rock, granites, mica chert, and microquartzite attests either to the continuing introduction of material of the Tuva-Mongolian mass, or to erosion of deposits of the Bayan-Kol suite. Heavy weathering of a significant portion of the clastogene components in both the Uzunsair and in the Bayan-Kol suite confirm the existence of a warm and humid climate at this time.

The deposits from the Uzunsair suite in the northern syncline were built up under deeper-water conditions, with the lower part of the shelf representing the upper part of the continental slope. Under these conditions the silty-clayey sediments, and sometimes finely sandy sediments that exemplify different types of facies, underwent preferential development. Products from the erosion of basic and intermediate volcanites played the principal role in the accumulation of terrigenous sediment, while products from the erosion of perclitic volcanites and metamorphosed rock played a secondary role.

Periods of terrigenous sedimentation alternated with periods of intensive subaqueous volcanism accompanied by the formation of pillow lava of a basic and medium composition, as well as products of subaqueous disaggregation of the latter. Volcanic activity on the proximate land produced ash material that could be used in the accumulation of the tuff horizons. Accumulation of carbonate deposits occurred at times when subaqueous volcanism was dormant and when the supply of terrigenous material had slackened off. The low thickness of the limestone underscores the brief duration of these types of conditions. The presence in the midst of the silty-clayey sediment of rounded limestone and volcanite pebbles, along with lumps composed of alternating layers of conglomerate, gritstone, and siltstone which had migrated from shallow-water sectors of the shelf is evidence of the comparatively steep gradient of the subaqueous topography and, possibly, of seismic phenomena.

Though deposits from the Uzunsair suite of the northern and of the southern syncline are in immediate proximity, the conditions under which they were built up are quite different. This, it would appear, is a consequence of tectonic contact between blocks which had once been at great distances from each other, but which characterized a common sedimentation basin. These types of relations are not at all rare in the case of folded, multiply dislocated regions such as Tuva [15].

The lithological and facial features of the Lower Cambrian complex found in the lower reaches of the Bayan-Kol River show that the deposits which are found here are characterized by three different types of sedimentation conditions: (a) shallow-water periodically drained zone of shelf with marked predominance of coarse-grained terrigenous sediments from an open, highly labile or bay-lagoon type of shoal and associated algal-archaeocyathian reefs or calcarenites (Bayan-Kol suite); (b) shallow-water shelf contiguous to a large land volcano with build-up of sediment from spontaneous flows under the conditions of restrictive evolution of tuff and reef-created formations (Uzunsair suite of southern syncline); (c) relatively deep-water sea with intensive subaqueous volcanism and heterogeneous predominantly silty-clayey sediments (Uzunsair suite of northern syncline).

In the first case terrigenous sedimentation occurred mainly as a result of a process of erosion of effusive periclastic rock, granitoid, and metamorphosed rock which had developed within the Tuva Mongolian mass, while in the second and third cases, as a consequence of the erosion of basic and intermediate effusive rock which had formed "local" volcanic edifices.

Data available in the literature [3, 10] show that in the other regions of central and western Tuva the Lower Cambrian deposits resemble in many ways the complex we have described and embrace bands of terrigenous sediment, basic and intermediate volcanite and tuffs of basic and intermediate volcanite, and horizons of reef-created limestone, all of varying thickness. The sections are characterized by significant variations in the relative proportions of volcanic and sedimentary formations (cf. Fig. 1). Sections in which clastogene sediments predominate have been discovered in the vicinity of the village of Ak-Durug, in the lower reaches of the Ezhim River, and southwest of Lake Syut-Khol. Roughly equal relative proportions of volcanites and clastogene sediment have been established north of the village of Ak-Dovurak; a marked predominance of basic and intermediate effusive rock, hyaloclastite, and tuff has been discovered to the north of the villages of Chadan and Teeli, near the peak of Mount Argalykty, and in the lower reaches of the Ak-Sug River.

Clastogene sediment is usually represented by coarse-grained, more rarely fine-grained flyschoid. Sharp variations in the relative proportions of fragments of basic and intermediate effusive rock and of effusive periclastic rock, silicon, quartz, and feldspar are observed; highly rounded ultrabasic [16] and limestone pebbles are sometimes also present. The latter are often represented by boulders and lumps several meters in thickness. The overall appearance of these pebbles is evidence that shallow-water sedimentation conditions are inherent to most of the regions.

The sea would appear to be characterized by a sea floor with dissected topography, abounding in numerous island and underwater volcanoes formed from great quantities of basic and intermediate effusive rock and pyroclastic rock, the disaggregation of which under subaerial and subaqueous conditions would have led to the formation of clastogene material. A significant quantity of terrigenous material entered from the Tuva Mongolian mass. The possibility is not excluded that sections typified by a marked predominance of andesitic and basaltic spherulitic lava and hyaloclastitic rock may be found in proximity to underwater volcanoes, and that sections in which coarse flyschoid plays a fundamental role, such as the Bayan-Kol suite, define the position of large underwater volcanoes. It is possible that sections with fine-grained flyschoid, such as in the Uzunsair suite of the northern syncline of the lower reaches of the Bayan-Kol River, are outliers of relatively deep-water sedimentation conditions. It is instructive that such a section has been discovered in western Tuva near Lake Syut-Khol, i.e., near the northern boundary of a region adjacent to an ancient ocean basin.

On the whole these topographical and paleogeographical conditions correspond to a sea basin within the limits of an island arc system, the existence of which within central and western Tuva points to certain tectonic schemes [1, 4, 14]. It is most probable that such a system had been a segment of a fringing sea adjacent to a microcontinent (the Tuva Mongolian mass). The significant volumes of terrigenous material which has entered from the latter mass presupposes the presence in the Tuva Mongolian mass of a system of rivers whose deltas would appear to have formed an important element of an ancient sea basin. The Bayan-Kol suite in the section along the Bayan-Kol River, which is composed mainly of products of the erosion of rock from a continental crust, is, possibly, a marginal part of this delta, reworked under the conditions typical of highly labile sea shoals.

Our lithological-facial and mineralogical-petrographical study of the Lower Cambrian deposits in the lower reaches of the Bayan-Kol River lead us to the following conclusions.

1. The deposits represent a genetically heterogeneous formation and embrace the facies of a shallow-water part of the shelf and a relatively deep-water sea (lower part of shelf – upper part of continental slope). The proximity of deposits from different facial zones observed in the Uzunsair suite would appear to be the result of the tectonic convergence of once disconnected blocks, an event that had occurred at later stages of development.

2. Two associations were established on the basis of the relative proportion of rock-forming components in the terrigenous rock: (a) feldspar-quartz or quartz-feldspar greywacke; and (b) volcanomictic greywacke. The first association, which forms the Bayan-Kol suite, appears to be the result of the extensive involvement of products of the erosion of [blocks from a continental-type crust] situated to the south of the Tuva Mongolian mass. The second association, which is confined mainly to the Uzunsair suite, but is also encountered in the Bayan-Kol suite, was formed as a result of the erosion of basic and intermediate effusive volcanite, which, in the Early Cambrian period, had become widely developed in this region.

3. In terms of the lithological features of the rock and the mineralogical and petrographical composition of clastogenic varieties, the section in the lower reaches of the Bayan-Kol River resembles in many ways sections in other regions of central and western Tuva, which leads us to conclude that the sedimentation conditions are the same throughout the entire territory.

4. The topographical and paleogeographical conditions present in the build-up of Early Cambrian deposits in central and western Tuva are fully in accord with existing data on the relation of this region during the Early Cambrian to an island arc system which separated the sea basin from an ocean-type crust situated in western Sayan, and a continental crustal block corresponding to the Tuva Mongolian mass.

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A new hypothesis is proposed for the formation of phosphorites, in which Vendian-Cambrian basins became stagnant and phosphorous was deposited biogenically.

The chemogenic hypothesis of phosphorite formation advanced by A. V. Kazakov [38-40] has long dominated the field of phosphate geology. The principal source of P_2O_5 was deep oceanic waters, which were transported by bottom currents and displaced coastal waters by upwelling. Phosphorites were then deposited along the shore by chemical precipitation of P_2O_5 from this supersaturated seawater.

Kazakov's hypothesis was largely based on a geochemical analysis of the present-day oceans, on physicochemical experimentation, and on information derived from phosphate geologists, obtained over many decades of research on phosphate deposits.

We attempt to resolve the problem of the origin of phosphorites in light of modern techniques; therefore we, like Kazakov, begin with an analysis of the geochemistry of phosphorous in the earth's crust.

Figure 1 is a diagrammatic section of the crust and hydrosphere according to the tectonic plate concept. It shows a two-layer crust under the ocean and a three-layer crust beneath the continent. Numbers indicate the total amount of P_2O_5 calculated for each domain. We derived the P_2O_5 for the oceans from data in Ronov and Korzina [49] and Horn and Adams [81]. The phosphorous pentoxide in various parts of the sedimentary cover, the granitic-metamorphic layer, and the basaltic layer was determined from data in Ronov et al. [50].

In examining Fig. 1, attention is drawn to the relatively small amount of P_2O_5 in the oceans ($2.2 \cdot 10^{11}$ tons). This is close to the amount of the total world resources, calculated by Yashin and Zharkov [76] as $4.58 \cdot 10^{10}$ tons.

The amount of P_2O_5 in the Earth's crust increases with depth. Sedimentary rocks on the continents and in the oceans contain $8.1 \cdot 10^{16}$ tons, the granitic-metamorphic basement $11.5 \cdot 10^{16}$ tons, and the basaltic layer, $3.67 \cdot 10^{17}$ tons. The amounts shown on the right-hand side of Fig. 1 are consistent with this trend. Basic gabbro and peridotite are clearly the principal sources of phosphorous, which is found in the mineral apatite. Doubtless in those cases where mantle rocks are erupted at the surface, and subsequently weathered and eroded, they are an important source of the phosphorous in nearby sedimentary basins.

Figure 1 also shows an estimate, based on Gordeev's data [25], of the amount of P_2O_5 in river discharge. We note that most of the phosphorous is transported in suspension ($4.67 \cdot 10^7$ tons of P_2O_5 per year); only 7% of the total phosphate is in solution, for an annual total of $0.37 \cdot 10^7$ tons.

This ratio of suspension to solution reflects the stability of apatite during weathering and subsequent transport. We emphasize that at the present time there is a maximum amount of phosphorous dissolved in river water, probably due to the widespread active mining of phosphorous for fertilizer for agriculture.

There can be no doubt that the amount of phosphorous in solution in the rivers was much less in the geological past than now, and this must be considered in estimates of resources.

Knowing the amount of phosphorous dissolved in the oceans and the annual supply of P_2O_5 by the rivers, it is easy to calculate the rate of renewal of this resource. Thus, accepting Horne's figure of about 90% P_2O_5 in solution in seawater

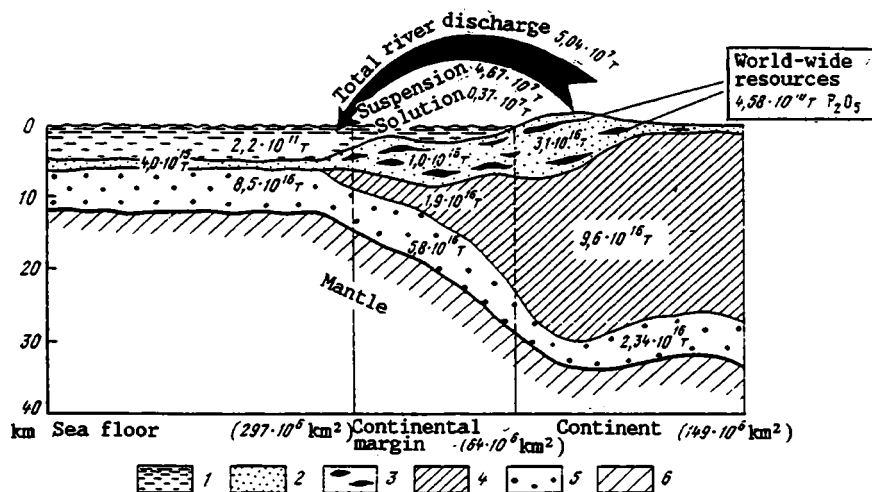


Fig. 1. Geochemical distribution of P_2O_5 in the hydrosphere and crust: 1) hydrosphere; 2) sedimentary cover; 3) phosphorite deposits; 4) granitic-metamorphic basement; 5) basaltic layer; 6) mantle. P_2O_5 content, %: sedimentary cover, 0.067 [5]; granitic-metamorphic basement, 0.07 [5]; basaltic layer, 0.15 [84], including gabbro, 0.24 [85]; peridotite, 0.05 [85]; basic peridotite, 0.38 [85]. Numbers indicate total amount of P_2O_5 according to [50] and [81]. Total river discharge and its content from Gordeev [25].

and only 10% in suspension [82], we use a value not of $2.2 \cdot 10^{11}$ tons, but of $1.98 \cdot 10^{11}$ tons of P_2O_5 . Dividing this by the annual amount of P_2O_5 supplied in solution by the rivers, we obtain 53,500 years, or about 50,000 years. This is the exact amount of time suggested by Barth [77] for the complete renewal of the phosphorous resources in seawater as a result of the sedimentary geochemical cycle.

It should of course be noted that many geologists and geochemists have calculated the period of renewal of dissolved phosphorous in the oceans. According to Ronov and Korzina [49] it is 160,000 years, and Baturin [4] proposed 200,000 years; our results are similar to those of Goldberg [24], who calculated it to be 48,000 years.

Using this period of renewal of P_2O_5 dissolved in the oceans, we can estimate the amount of ore that can be generated. This is particularly important inasmuch as the oceans apparently are now at the highest stage in the evolution of the hydrosphere, differing from the past in morphometric character and amount of water [57, 58], and thus may contain the maximum amount of P_2O_5 .

In order to resolve this question an absolute geochronology of phosphate ore formation must be clearly stated. It has been shown on the basis of data in [42, 48] that three major phosphate-bearing basins in Asia: Karatau (Kazakhstan), Khubsugul (Mongolia), and Yunnan (China), are located in deposits in the Tommotian, which lasted for 5 m.y. [83] to 10 m.y. [80]. We can thus calculate the amount of phosphorous that could be generated in modern oceans if all of the P_2O_5 resources were to be formed in these three basins.

Using the first figure of 5 m.y., and taking our rate of renewal of the phosphorous resources (50,000 years), it becomes obvious that the amount of P_2O_5 deposited cannot exceed 100 times the amount in the oceans; in other words, in this case the total paleogeographic resources of the three Asian basins can be estimated at $1.98 \cdot 10^{13}$ tons P_2O_5 .

Using the second figure (10 m.y.), the resources would be limited to 200 times the amount in the oceans, with resources of $3.96 \cdot 10^{13}$ tons P_2O_5 .

According to Bushinskii [19], Il'in [36], and Kholodov [66], the actual paleogeographic resources of the three phosphorite-bearing basins is $1.3\text{--}1.5 \cdot 10^{12}$ tons of P_2O_5 . This figure is undoubtedly too low, and does not take into account the numerous "embryonic" ore occurrences in the Cambrian of Kazakhstan, Mongolia, and China. It should be recalled that Yanshin and Zharkov [76] suggest that Vendian-Cambrian deposits on the continents contain about $1.41 \cdot 10^{16}$ tons of dispersed P_2O_5 , almost 20% of all the phosphorous in the sedimentary rocks of the world.

Even the modern oceans obviously cannot produce such a huge amount of phosphorous; it is doubtful that the hydrosphere at the Precambrian-Paleozoic boundary, when shallow seas predominated, had this much regenerating capacity.

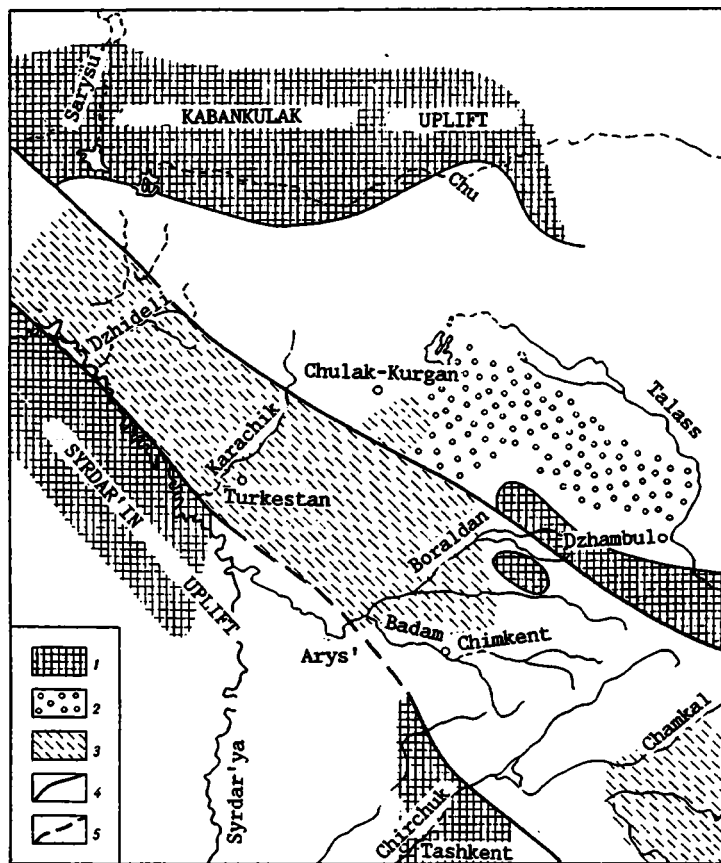


Fig. 2. Paleogeographic map of Karatau (Kazakhstan) during the Tommotian: 1) Precambrian uplifts, forming land areas; 2) phosphorites and phosphorite-bearing siliceous, clayey, phosphatic rhythmites; 3) rhythmically bedded carbonaceous, siliceous, clayey, carbonate-bearing deposits; 4) faults; 5) inferred fault.

Thus, according to these rough estimates the oceans could not have supplied the concentrations of phosphorous even in the three Asian phosphorite basins. Meanwhile, speaking of phosphorite deposits of that age, it should be kept in mind that we are not just dealing with individual phosphorite regions, but with an entire epoch of phosphate, ferromanganese, and metalliferous shale ore formation on nearly every continent at that time [1, 19, 23, 60-63, 65-70, 75].

Ore components deposited in Vendian–Cambrian seas were formed as a result of rapid weathering and erosion of unusual source areas, mainly basic to ultrabasic and alkaline intrusions containing P, V, Co, Ni, Fe, Mn, and other elements, Early Proterozoic iron–manganese jaspilite belts, and locally Archean basaltoids [68].

Most of the ore components were mobilized on the continents and migrated into adjacent basins, mostly in suspension. Phosphorous was apparently no exception, and fine suspended material enriched the deeper parts of the Vendian–Cambrian seas.

The Karatau phosphorite basin (Kazakhstan) is the best example of an ancient phosphorite deposit. The Karatau region was a very important location of phosphorite formation. Five major deposits of fine-grained phosphorites (Zhanatas, Kokdzhon, Koksus, Aksai, and Chulaktau) and more than 30 small and medium phosphate deposits are located in this basin over an area of 2500 km² (120 × 25 km).

All of the phosphate mineralization is controlled by the Chulaktau suite, identified by numerous hyolithids, chitelmints, tommotiids, conodonts, anabaritids, and other fossils of the Tommotian Stage of the Lower Cambrian [44].

The phosphorite suite is underlain by the Berkutin dolomite, which has been referred to the Vendian [41] and to the Lower Cambrian [35]. Since phosphorite-bearing beds and lenses have been found in different parts of the Berkutin, with lumps and fragments of phosphorite, while conglomerates at the base of this unit overlie Karoi rocks with traces of erosion, we consider this formation to be Tommotian.

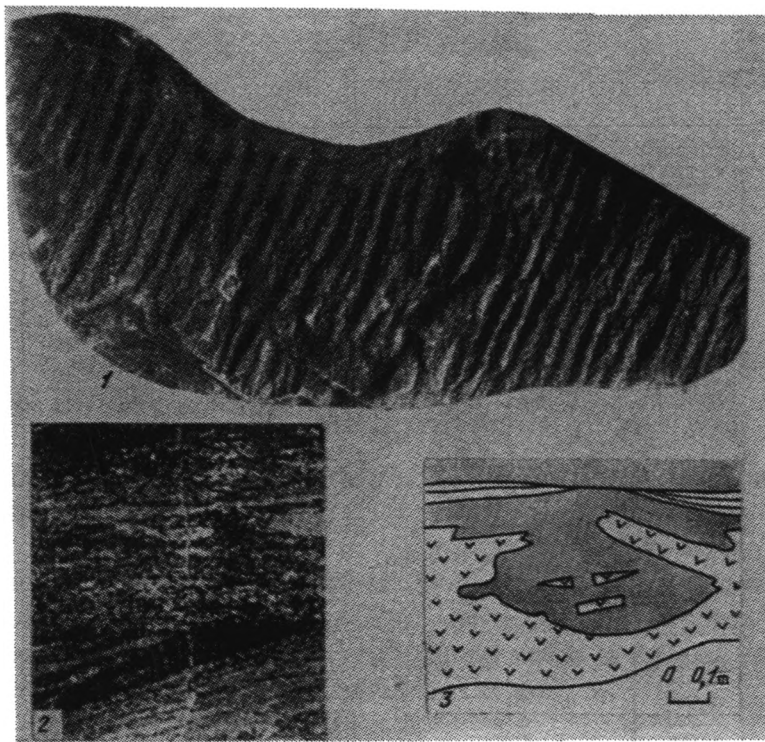


Fig. 3. Structures in rocks of the Chulakta suite, Little Karatau range: 1) Ripple marks in phosphorite from the Karashat ore deposit (2/3 actual size); 2) cross-bedding in phosphorites from the Dzhanatas ore deposit (2/3 actual size); 3) sketch of erosional wash-out refilled with phosphorite (gray) and siliceous phosphatic rock (pattern), Berkuty ore deposit.

Phosphatic deposits in the Little Karatau region are overlain by the thick Shabakhtin carbonate suite belonging to the Lower, Middle and Upper Cambrian and extending into the Ordovician [34].

The tectonically complex Little Karatau contains the northeastern flank of a major Proterozoic anticlinorium with large thrust faults. The Bol'shekaroi, Malokaroi, Aksai, and North-Berkutin valleys lie along these faults, which generally have phosphorite-bearing Chulakta deposits on their northeast sides. These are cut by east-west and north-south normal faults, which divide up the ore deposits and create a checkerboard of tectonic blocks and isolated slices.

A dense northwest-trending system of faults bounds the Little Karatau on the southeast and separates it from the Great Karatau. The latter is a long and complex meganticlinorium composed of highly faulted Proterozoic, Caledonian, and Hercynian belts of rocks. Three large lower-order anticlinoria, the Northwestern Karatau, Baydzhansai, and Boroldai, are separated by two other anticlinoria, the Central and Bugun' [22, 43].

Here the Kurumsak suite is the stratigraphic equivalent of the phosphorite-bearing Chulakta suite of the Little Karatau. It contains rhythmically bedded silicified shales, clay shales, and limy shales enriched in U, V, Co, Ni, Mo, Se, Re, and other elements; barite-bearing rocks occur in the upper part of the section [2, 32, 33, 62].

Paleogeographically, the lower Cambrian sea located in the Great and Little Karatau area was a narrow, shallow strait-like body of water that extended from southeast to northwest. The land areas were the Syrdar'in massif, the Kaban-kulak uplift, and possibly the Chuilii massif, and on all sides the Kokdzhot horst, which apparently was also above sea level (Fig. 2).

Rhythmically bedded carbonaceous, siliceous, clay shales were formed in the deepest parts of the paleobasin, often interbedded with carbonaceous carbonate and siliceous shales. The siliceous components of these deposits contain vast quantities of radiolarians, and the rhythmic accumulations of saproplanktonic remains apparently reflect seasonal blooms and collapses of the plankton.

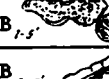
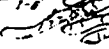
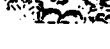
Distinct morphology			Indeterminate			
A	B. Microphytolites					uncertain affinities
	oncolites		microstromatolites	compound algal colonies		
	internal structure					
	complex	absent				
						
						
						
						
						

Fig. 4. Phosphatic forms in rocks of the Chulakta suite, Little Karatau range.

The Kokdzhot horst, surrounding the deeper water areas on all sides, is a system of submarine shoals; here, in an area now occupied by the Little Karatau, are at least three east – west trending submarine uplifts separated by two relatively shallow lagoonlike basins. The phosphorite-bearing deposits proper formed in these.

Two types of phosphorite deposits are readily recognized. A rather thick rhythmically bedded carbonaceous, siliceous, clayey sequence with beds and lenses of nearly monomineralic phosphorite are developed in the deeper parts of the basins. Thinner beds and lenses of phosphorite with relict algal and bacterial structures occur on the adjacent uplifted shoal areas; these include phosphatic oncolites of the genus *Ozagia* and various macroscopically dissimilar stromatolites. Here the normally thick Chulakta suite has been thinned to several tens of meters and it is common to find cross-bedding, ripple marks, shoreline erosion features, worm burrows and tracks of other mud-eaters, and desiccation cracks – shallow water features that are typical of Karatau phosphorites (Fig. 3).

The nature of the phosphate particles making up the beds and lenses of phosphorite in the siliceous and carbonate-bearing rocks of the Chulakta suite is a very interesting problem. Previous workers have offered a number of opinions. For example, Tushina [59] considered the phosphate grains to be typical microconcretions, Bushinskii [19] called them phosphatized coprolites, and Eganov [31] suggested that they are typical intraclasts. Kholodov concluded that phosphatic microlaminae "... are biogenic algal forms of a type of solitary stromatolite" [62, p. 35].

We have examined 600 thin sections that characterize the Chulakta suite in nine phosphorite deposits and prospects in the northwestern Karatau. Sections in the Berkuty Severnyi, Koks, Kistas, Baba-Ata, Kesiktube, Dzhannatas, Berkuty I, Dzhanlan, and Ala-Dzhar regions were systematically sampled over 0.5-1.0-m intervals. Three morphological groups of phosphate particles in the phosphorite deposits were distinguished (Fig. 4).

The first group (A) includes numerous microfossils composed of pelitomorphous phosphatic material; they have spiral cylindrical or chainlike shapes, commonly resembling empty containers and various coccolidal forms. In phosphatized parts of the Chulakta biota, Sergeev and Ogurtsova [51] described *Obruchevella parva* Reitlinger, *O. delicata* Reith., *O. cf. meischucunensis* Song., *Eomycetopsis robusta* Schopf et Knoll, *Golubic*, *Palaeotubulus* aff. *lamellosus* Wang, *Eophanocapsa molle* sp. nov., *Tetraphycus ampilis* Golovenok et Belova, *T. acutus* sp. nov., *Archeophycus venustus*, *Oseillatoropsis* sp., *Myxococcoides grandis* Horodyski et Donaldson, *Siphonophycus* sp. and others.

These forms are no doubt the products of biologic activity of *Spirulina* blue-green algae.

The second group (B) includes phosphatic particles whose internal structure is closely related to their morphology; as a rule, they are round, oval, tetrahedral, or sporelike bodies enclosed within an enveloping cover. They form rounded, oval, trigonal, club-shaped, lance-shaped, or spindle-shaped clasts of various sizes from a fraction of a millimeter to several millimeters (B_{1-1} , B_{1-6}). Figure 5 shows photomicrographs of these particles. In addition to these, particles were found that had no distinct internal structure (B_{1-1} - B_{1-6}).

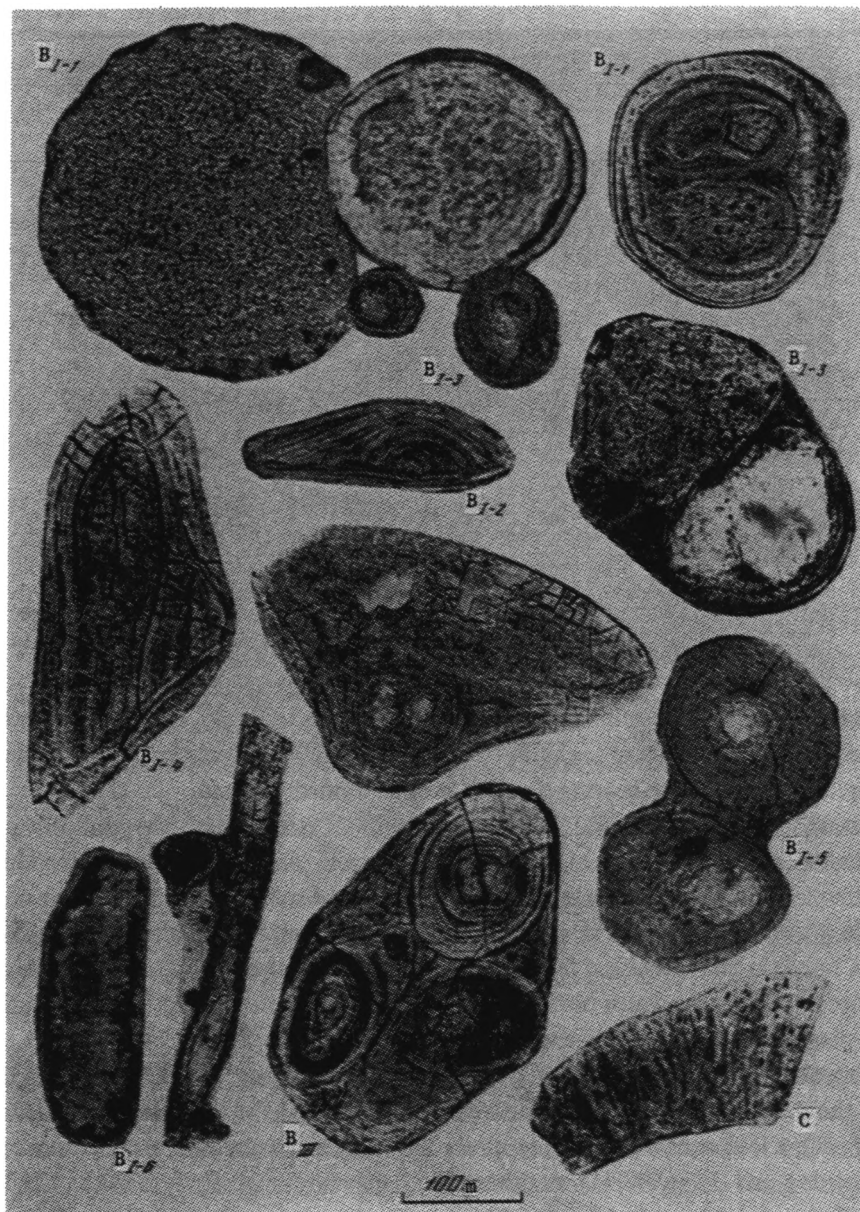


Fig. 5. Photomicrographs of phosphatic particles in groups B_{I-1} - B_{I-6} , B_{III} , and B in siliceous, limy, phosphatic rocks of the Chulakta suite, Little Karatau.

The principle of "parentage" is evident in particles in group BI; the same form of phosphate can differ quite considerably in size in beds of different lithology. One can thus easily construct a number of situations in which a certain type of particle would form a sequence "from minute to huge." This feature of the group BI particles suggests that they are biogenic in origin.

The phosphate particles with internal structures resembling microstromatolites or compound algal colonies make up a special grouping (B_{II} - B_{III}). As a rule, these forms are closely controlled by the external shape of the grains, suggesting scraps of phosphatic algal mats.

Group C consists of phosphatic particles of uncertain affinities. It usually makes up only 10-12% of all the phosphatic particles, and is a minor component: 88-90% of the phosphatic material in phosphorite beds probably is of bacterial or algal origin. Rozanov and Zhegallo [48] quite rightly emphasize the importance of biogenic factors in Cambrian sedimentation.

TABLE 1. Distribution of Phosphorous in Present-Day Seas and Oceans, mg/liter

Sea	Water					
	surface	deep	reference	mud		reference
				from-to	average	
Caspian						
Northern	0,0-35,0	-	[8]	220-8429	1240	[14]
Middle	0,1-15,0	8,0-75,0	[8]	37-119	24-200	[15]
Southern	0,1-17,0	7,0-78,0	[8]	24-550	25-360	-
Azov	0,0-22,0	4,0-200,0	[6, 30]	Trace-4800	920	[26, 28]
Black	7,0-40,0	107,0-299,0	[17, 30, 10, 13, 52, 79]	80-740*	260	[21]
				270-1570**	920	[21]
				550-1160***	840	[21]
				200-5000	230-2300	[27, 29]
Baltic (basin)						
Gotland	5,3-14,0	28,0-300,0	[74]	-	-	-
Landsort	7,1-7,8	13,0-85,0	[74]	-	-	-
Atland	9,0-10,0	10,0-20,0	[74]	-	-	-
Barents	6,0	20,0	[9]	40-990	245	[73]
Okhotsk	0,0-20,0	60,0-100,0	[18, 45]	180-360	-	[11, 12]
Pacific Ocean	0,0-46,0	60,0-105,0	[4]	4-1960	330	[16]
					(gray terrigenous muds)	
					Trace-670 (red muds)	

*In Recent deposits.

**In ancient Black Sea deposits.

***In new euxinic deposits.

It is now clear that the most important facies of the Karatau phosphorites were created by two competing processes: bacteria-algal structures and sorting by waves, destroying these colonies and redepositing the poorly sorted debris on the sea floor.

The mechanism by which P_2O_5 was extracted from the seawater is not yet completely understood, although one thing is clear: it was closely associated with biological activity.

It can be assumed that under conditions of increased amounts of phosphorous dissolved in the seawater, the original bacterial-algal carbonates were altered instantaneously, in geologic terms, to phosphates. This is supported by a thermodynamic analysis of the reaction



which at 1 atmosphere is exothermic and shifts to the right toward the formation of $Ca_3(PO_4)_2$ or other calcium phosphates [46].

It is no less probable that bacterial activity in the near-shore facies brought about mineralization of the organic phosphate components through its absorption by the living bacteria-algae association in the form of nucleic acid, lecithins, phytin, phospholipids, and other compounds enriched in P_2O_5 .

It is also possible that the two processes took place at the same time and were responsible for the formation of the bacterial-algal deposits.

In addition to the mechanism of extraction of phosphorous from the Cambrian seas, there was a mechanism for the enrichment of the waters in dissolved phosphates. This is achieved in modern seawater by stagnation and the production of hydrogen sulfide.

The Black Sea is widely regarded as a typical hydrogen-sulfide-bearing basin; below the 200 m oxygenated layer with a salinity of 1.8‰ is a stagnant zone 2000 m thick with dissolved hydrogen sulfide and a salinity of 2.2‰. The H₂S content increases here from 0.52 mg/liter in the upper part to 7.5 mg/liter at the bottom, with remarkably little convectional mixing [20, 47, 54, 56, 71].

Most investigators consider the origin of the hydrogen sulfide to be related to the breakout of the Mediterranean Sea through the Bosphorus into the ancient freshwater Black Sea basin, with intensified development and destruction of plankton and consequent outbreak of the activity of sulfate-reducing bacteria in the muds [58].

Skopintsev and Karpov [53] and later Fonselius [79] have shown that hydrogen sulfide-bearing water from the Black Sea contains significant amounts (25-225 µg/liter) of phosphorous in solution. Fonselius' equilibrium calculations show that there is $1.4 \cdot 10^8$ tons of P₂O₅ in 537,000 km³ of water from the Black Sea. Since this volume of seawater usually contains only $0.56 \cdot 10^3$ tons of P₂O₅, it is obvious that hydrogen sulfide actively promotes the solution of phosphates.

Inasmuch as ready reserves in the Karatau phosphorite basin are estimated to be $5.04 \cdot 10^8$ tons of P₂O₅, it can be concluded that the Black Sea contains 1/3 of this amount.

The distribution of phosphorous in the waters of present-day seas and oceans is presented in Table 1. Some important conclusions can be drawn from these data.

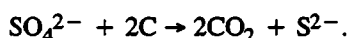
1. An increased phosphorous content in deep marine waters is always present in basins with hydrogen sulfide; as shown by Baturin [4], the phosphorous content in stagnant basins commonly reaches 300 µg/liter (Black Sea, Baltic Sea, Norwegian fjords, etc.).

2. The amount of phosphorous in solution in seawater increases irregularly downward; it is lowest where plankton is abundant, and greatest in the depths of the basin.

3. The greatest amount of dissolved phosphorous is found in muddy waters, where it is associated with buried organic material; in fact, the phosphorous content in gray terrigenous muds of the Pacific Ocean reach 330 µg/liter, while deep red clays devoid of C_{org} contain only 24 µg/liter.

It is quite obvious that the main process responsible for the solution of phosphorous is the diagenetic activity of various bacteria, which thrive in the muds on the sea floor and are closely regulated by the amount of buried organic material.

With respect to Strakhov's work [54-65], aerobic bacteria are active in the first stage of diagenesis, oxidizing and decomposing organic matter; this produces CO₂ followed by H₂, NH₃, CH₄, and other components. Later on, in an anaerobic environment, sulfate reducing bacteria extract SO₄²⁻ from seawater and reduce sulfur by



Hydrogen sulfide and carbon dioxide are formed and promote the solution of phosphates and, apparently, even apatite. Phosphates in solution in mud may not only form phosphorite concretions, but also, as shown by Bruevich and others [18], may enter bottom waters and markedly enrich them.

Facies and geochemical analyses of the rhythmically bedded carbonaceous, siliceous, clayey carbonate-bearing facies in the deeper parts of the Karatau basin suggest a quiet, undisturbed environment. It is important to note that these beds contain 2-5 to 20 or even 50 percent carbonaceous material, which occurs in the form of graphite or anthraxolite; the carbonaceous beds are no doubt relict saproplanktonic material. The importance of plankton in the formation of these Cambrian deep-water sediments is indicated by abundant siliceous radiolarian fossils [3, 62].

The degree of diagenesis in the muds of the Cambrian basin is indicated by the abundance of various sulfide minerals, including bornite, chalcocite, covellite, pyrite, sphalerite, molybdenite, sulvanite, arsenopyrite, pyrrhotite, and natronite. Fine phosphate concretions and nodules have been found in vanadium-bearing silicified shales [3].

The presence of hydrogen sulfide in the Cambrian basins is indicated by the lack of a benthonic fauna. This is typical of modern marine basins of the Black Sea type.

In order to finally resolve the problem of the composition of the water in the Cambrian basins, we have attempted to use the so-called coefficient of stagnation, which has been applied in the case of Tertiary deposits of the Caucasus area and Holocene sediments of the Black Sea [72]. A section with a high Mo/Mn ratio that was apparently, according to paleoecological indicators, deposited in a hydrogen sulfide environment has been found in the region of the Novogroznen

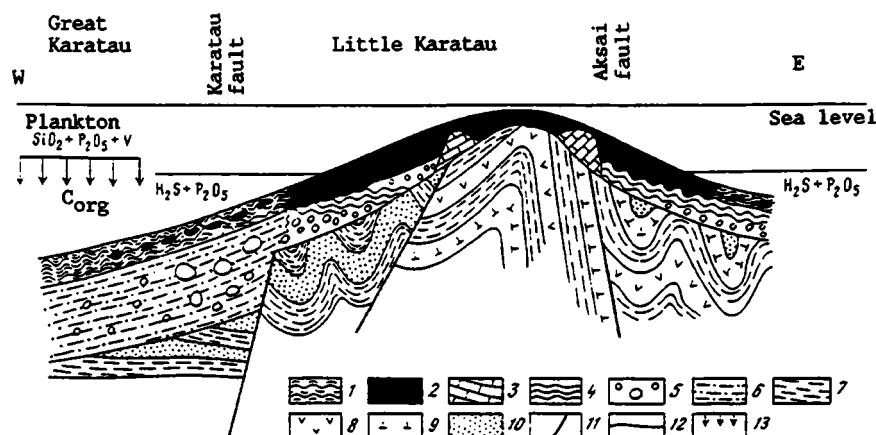


Fig. 6. Diagram Illustrating Sedimentation in the Karatau during the Early Cambrian: 1) rhythmically laminated deep-water carbonaceous, siliceous, shaly, limy sediments; 2) phosphorites; 3) Berkutin dolomite; 4) dolomite olistoliths and bioherms; 5) blocks in tillitelike deposits; 6) terrigenous shales; 7) clay shales; 8) cherty and siliceous rocks; 9) tuffites and volcanoclastic rocks; 10) sandstones and siltstones; 11) faults; 12) boundary between hydrogen sulfide waters and oxygenated waters; 13) planktonic sedimentation.

and Maikop deposits. This ratio was studied in Chokrak and Karagan black shales, which in the opinion of paleoecologists was formed in well-aerated waters. It turns out that where stagnation occurs, the ratio of molybdenum to manganese ranges in the hundredths, but with the transition to well aerated water, it decreases to the thousandths.

Our studies of the Mo/Mn values in the Cambrian rhythmites in the carbonaceous, siliceous, clayey deposits of the greater Karatau have shown that the range there is 0.05-0.15, which strongly suggests that they were formed in stagnant conditions with an ample supply of hydrogen sulfide in the bottom waters. This suggests in turn that along with H_2S , the sea floor muds had a rich supply of dissolved phosphorous.

The complete phosphorous cycle in Cambrian marine basins took the following form. The Karatau shallow marine basin, like many other Vendian-Cambrian basins (Khubsugul, South China, Australian, West African, and others), received an abundance of phosphate compounds from the land, transported in solution or as a fine suspension, as a result of the following: 1) a tectonomagmatic event in the pre-Vendian that provided a widespread source of supply in ultrabasic rocks, introducing a large amount of P_2O_5 into the weathering zone; 2) a previous period of intensive weathering; and 3) a complete peneplanation of the topography, which caused a reduction in the amount of clastic terrigenous and carbonate material in the sediment supply [64, 67, 68].

The increased supply of P_2O_5 from the land caused an explosion of plankton. This phyto- and zooplankton bloom was reflected in the formation of rhythmically bedded deep-water carbonaceous, siliceous, clayey laminae in the pelagic areas of the seas. These sediments also accumulated phosphorous, vanadium, cobalt, nickel, molybdenum, and other metals, which were absorbed by organic matter in the sediment or deposited from suspension. The rhythmic deposition was caused by seasonal fluctuations in the production of the plankton.

Microbiological decomposition of the organic matter in the rhythmically laminated deep-water muds, and the activity of sulfate-reducing bacteria, produced a surplus of diagenetic hydrogen sulfide and carbon dioxide in the sediments, and thus in the bottom waters as well. This geochemical process can be seen in modern and ancient Black Sea deposits.

During oxidation of organic matter and microbiological sulfate reduction, fine phosphatic material was dissolved and enriched the bottom waters where hydrogen sulfide was being introduced (Fig. 6).

Cyanobacteria colonies flourished in well aerated warm waters on shoals in the Cambrian Karatau seas, near the boundary of the oxygenated and hydrogen-sulfide-bearing waters. Large amounts of hydrogen sulfide dissociated under the effect of oxygen, sharply decreasing the solubility of P_2O_5 and creating biochemical conditions favorable for the deposition of phosphatic material.

Algal-produced stromatolites interfered with wave action on the shoals. Mechanical breakup of the phosphatic material was followed by redeposition, forming beds and lenses of phosphorite that entered into the overall rhythmic sequence of carbonaceous, siliceous, and carbonate material.

It is curious that the shoal areas of the Little Karatau basin varied in depth over time, apparently gradually filling up with biogenic and chemogenic material. In pre-Tamdin time a complex system of intermittently dry pools were established in which phosphatic, iron- and manganese-bearing, carbonate-bearing bacterial mats with microfossils and stromatolites were formed.

It has become clear that Vendian–Cambrian phosphate formation took place in shallow seas where sedimentation was quite different in every way from the present oceans. Phosphorous deposition on shoals was mainly biogenic, and the paleogeographic conditions are completely inconsistent with the upwelling hypothesis, although the latter appears to be quite agreeable and attractive to many well-known experts [4, 37, 78].

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